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Thermal analysis in the research on materials for energy conversion

Agersted, Karsten

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Thermal analysis in the research on materials for energy conversion

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Risø Campus
Technical University of Denmark

DTU

- Inaugurated 1958 as a National Laboratory

- Since 2008, part of the
  Technical University of Denmark

- Research on energy related technologies, e.g.
  - Wind turbines
  - Fuel cells
  - Biofuels
  - Solar cells
  - Hydrogen storage
  - Batteries
  - Energy systems

- ~600 employees

Department of Energy conversion and storage

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  - Wind turbines
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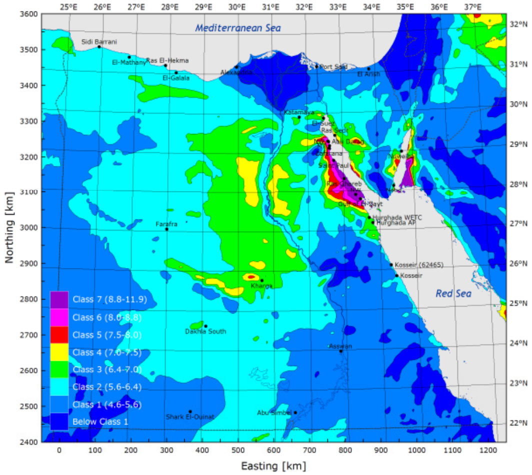
  - Solar cells
  - Hydrogen storage
  - Batteries
  - Energy systems
- ~600 employees

- **Test facility for large wind turbines**
- **Composite materials**
- **Wind atlas**



Department of Energy conversion and storage

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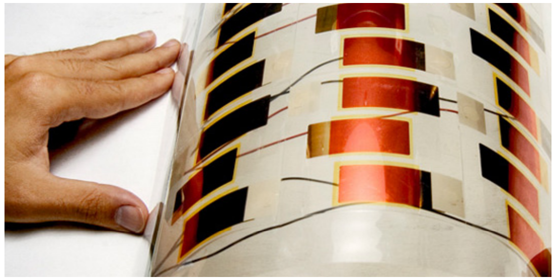
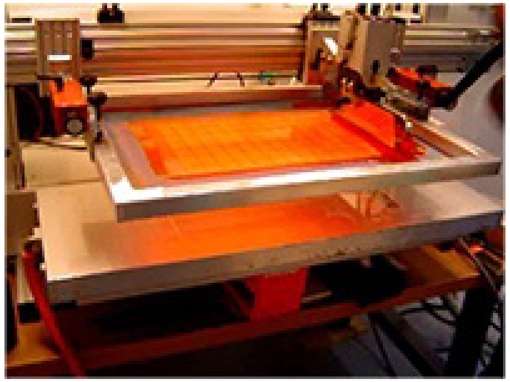
  - Wind turbines
  - Fuel cells
  - Biofuels
  - Solar cells
  - Hydrogen storage
  - Batteries
  - Energy systems
- ~600 employees

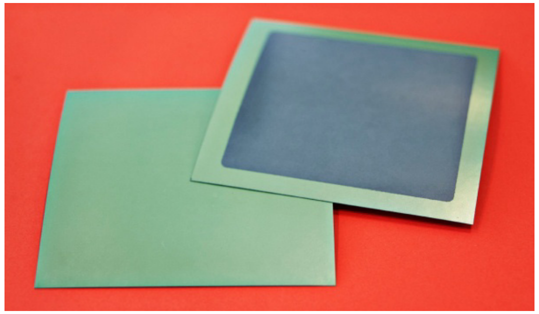
- **Polymer solar cells**
- **Produced by screen printing**
- **Flexible and cheap**



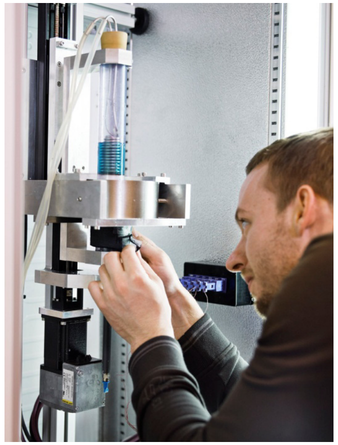


Department of Energy conversion and storage

Technologies

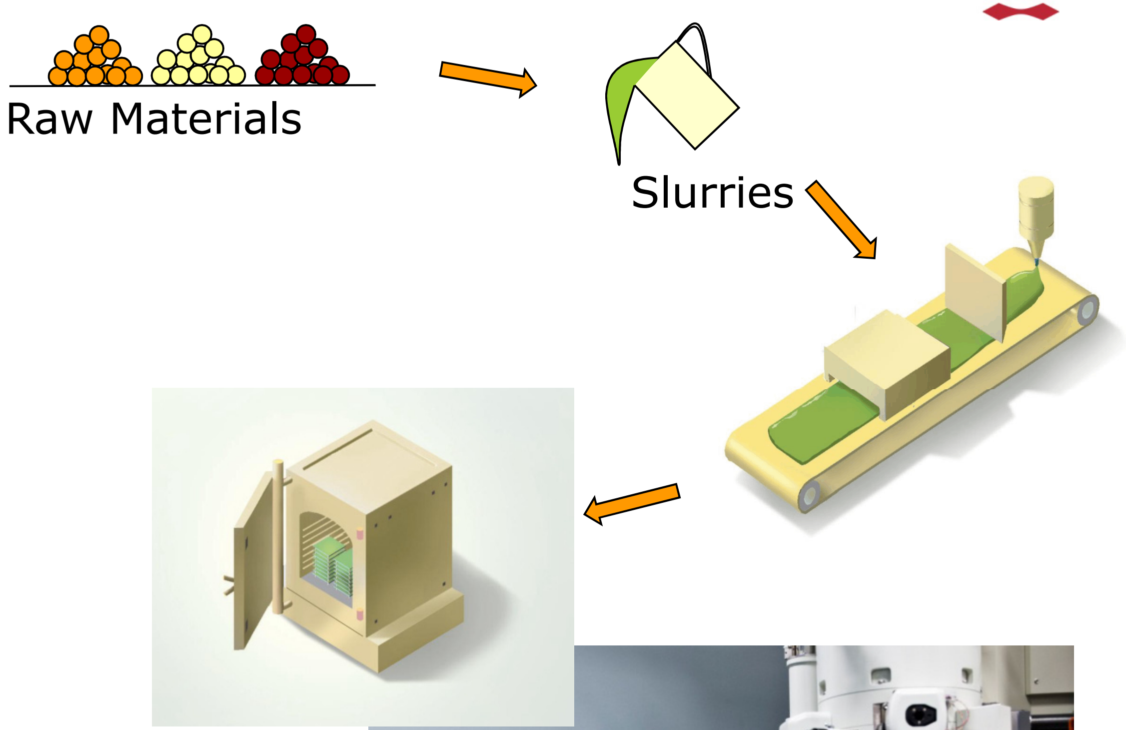


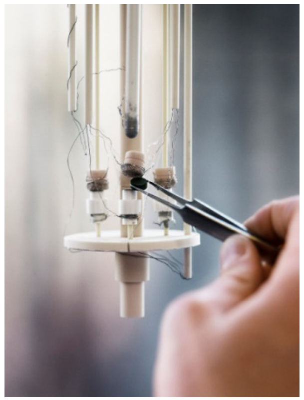
- Solid Oxide Fuel Cells
- High temperature electrolysis
- High temperature PEM fuel cells
- Polymer Photo Voltaics
- Magnetic refrigeration
- Membranes for oxygen or hydrogen separation
- Flue gas purification
- Thermoelectrics
- Batteries
- Hydrogen storage

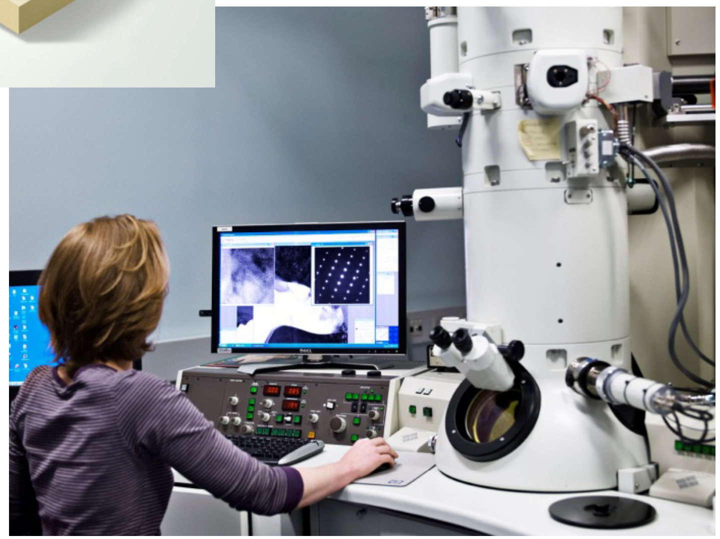


Research on solid oxide materials

- Ceramic processing
- Materials development
- Characterization
- Testing in-situ
- Modelling







Typical use of thermal analysis @ Risø DTU

- Dilatation, sintering shrinkage and profile characterisation, warping during processing

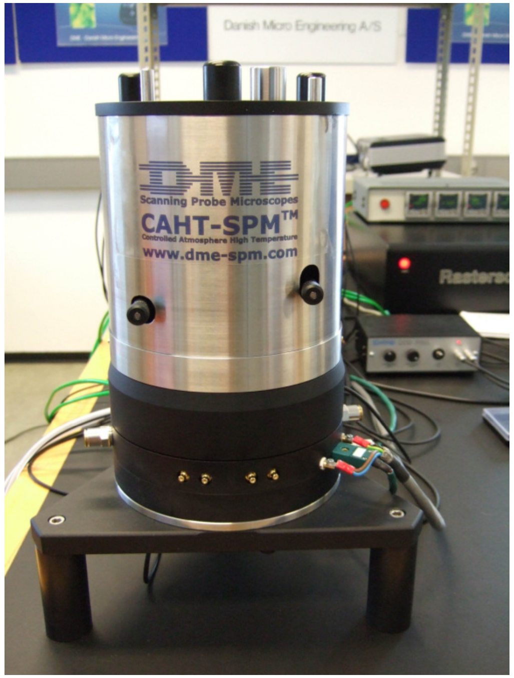
- Thermogravimetry and dilatometry with complex thermal profiles, eg:
  - Binder removal, sintering, thermal decomposition
  - Reactivity with different atmospheres,
    - Corrosion
    - Oxygen stoichiometry.

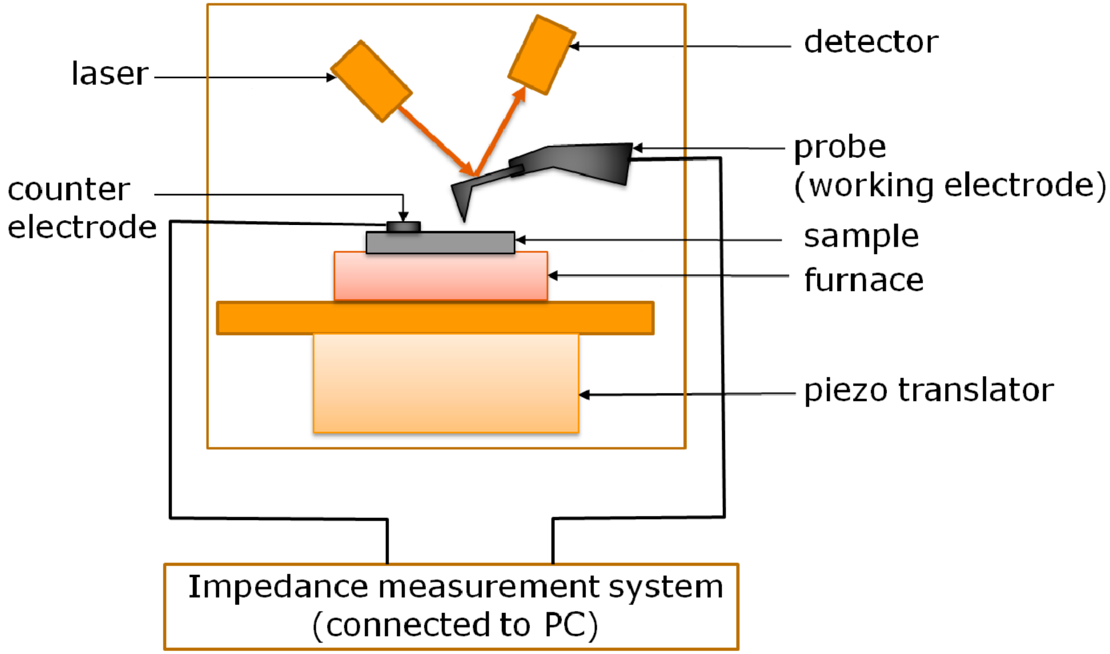
- Glass transition, crystallisation

- Determination of heat capacity, thermal conductivity, Seebeck coefficient

- High temperature XRD

CAHT-SPM





Contact measurements

”Controlled atmosphere”

Up to 650-700ºC

Contact and non contact measurements

Kelvin probe (surface potential)

Controlled atmosphere – pO_2 monitor

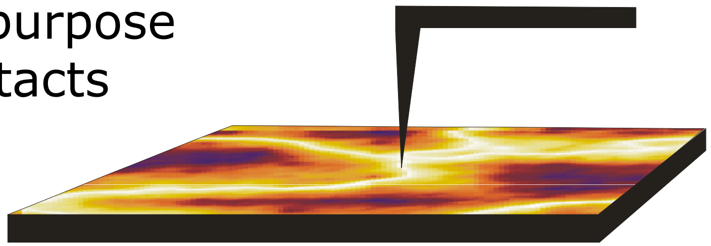
Up to 850ºC

Contact: Karin Vels, karv@dtu.dk

Purpose of the CAHT-SPM

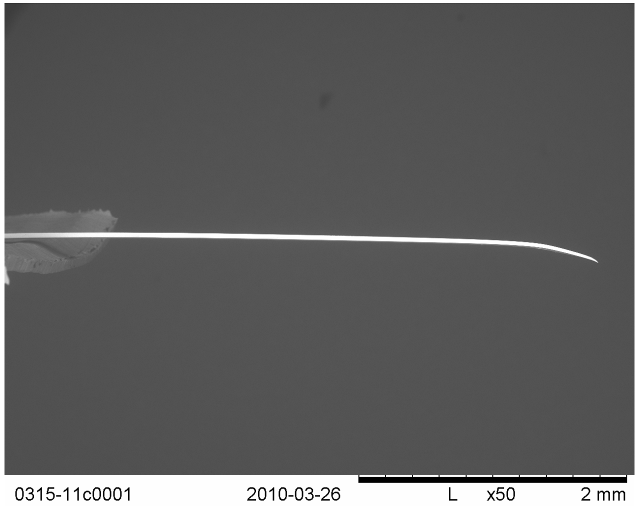
We want to probe local electrochemical properties ($1\ \mu m^2$ or smaller) in-situ in SOC electrode or other materials (> 600°C) and in a controlled atmosphere

Custom made probes are essential for the purpose of the CAHT-SPM eg. for studying contacts between electrode materials



Probe properties

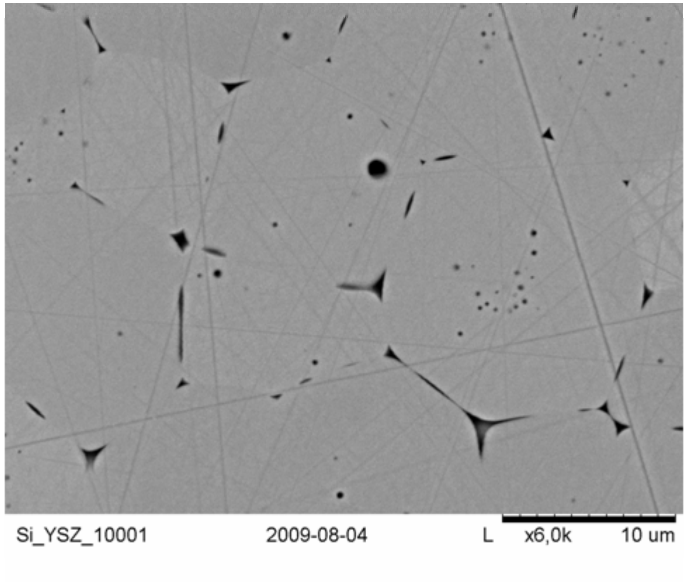
- Stable at high temperatures
- at reducing and oxidising conditions
- electrically conductive



At the moment, probes are from

- Ceramics: LSM/YSZ
- Platinum-iridium

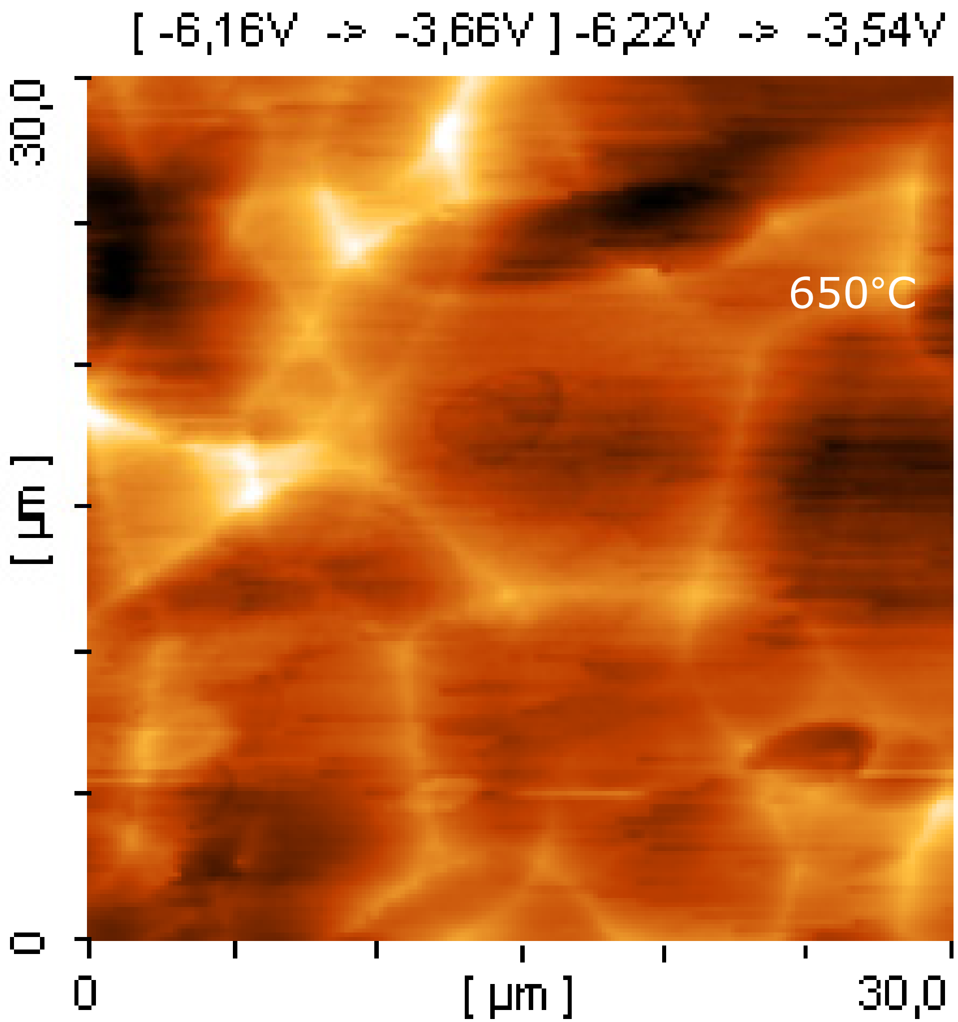
Si impurities in YSZ grain boundaries



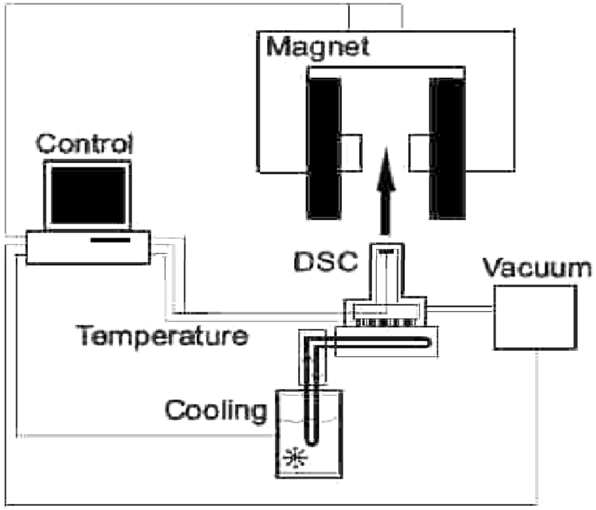
YSZ with 1000 ppm, sintered and polished

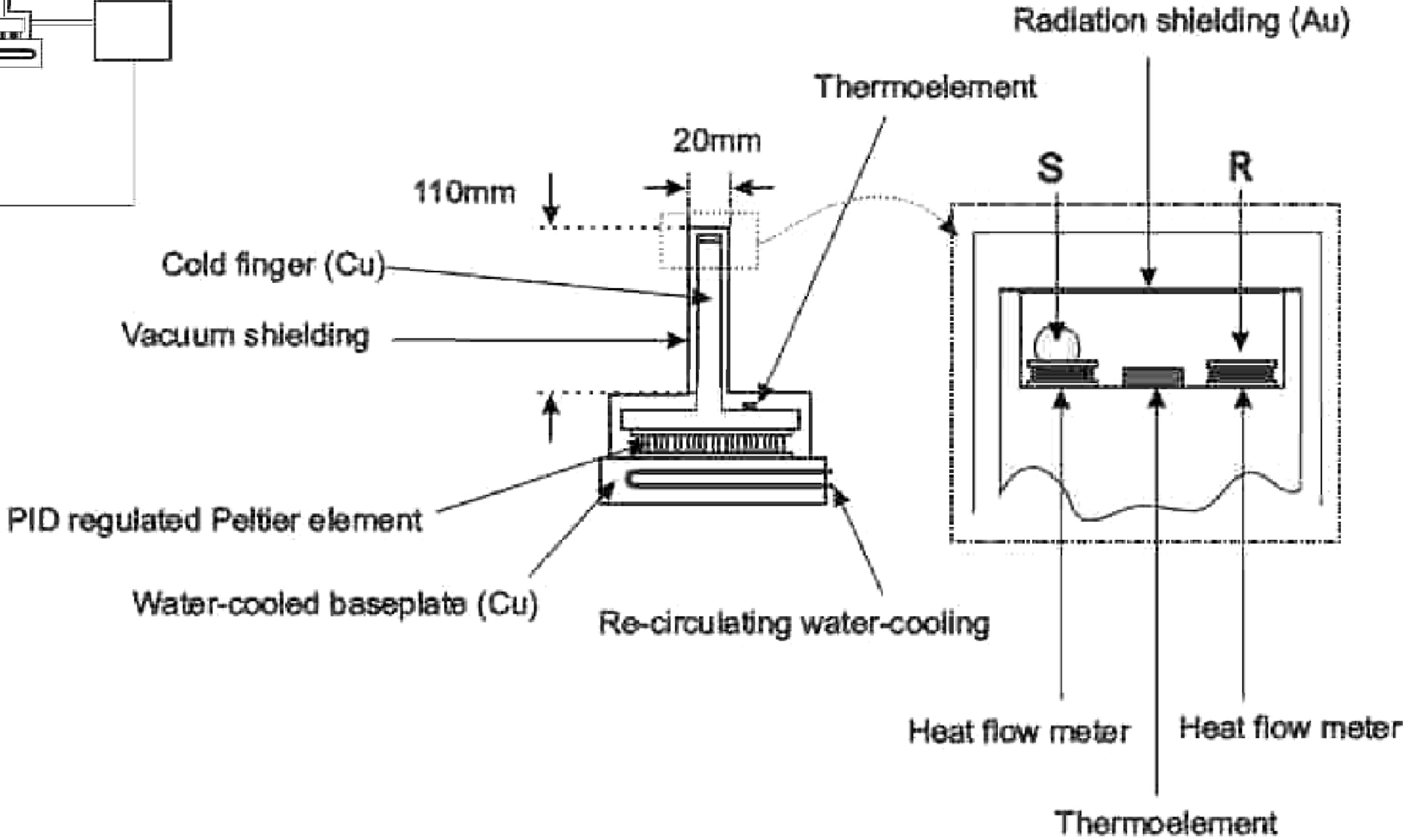
Dark = high conductivity,

White = low conductivity



DSC for indirect measurement of the magnetocaloric effect

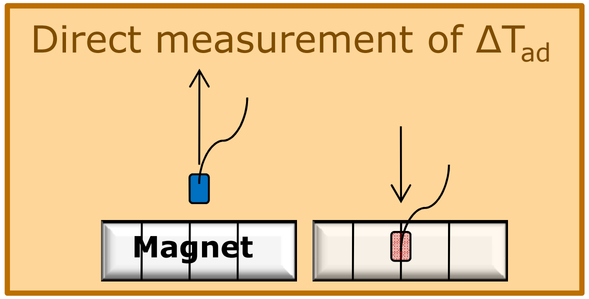




S. Jeppesen et al. REVIEW OF SCIENTIFIC INSTRUMENTS **79** (2008) 083901

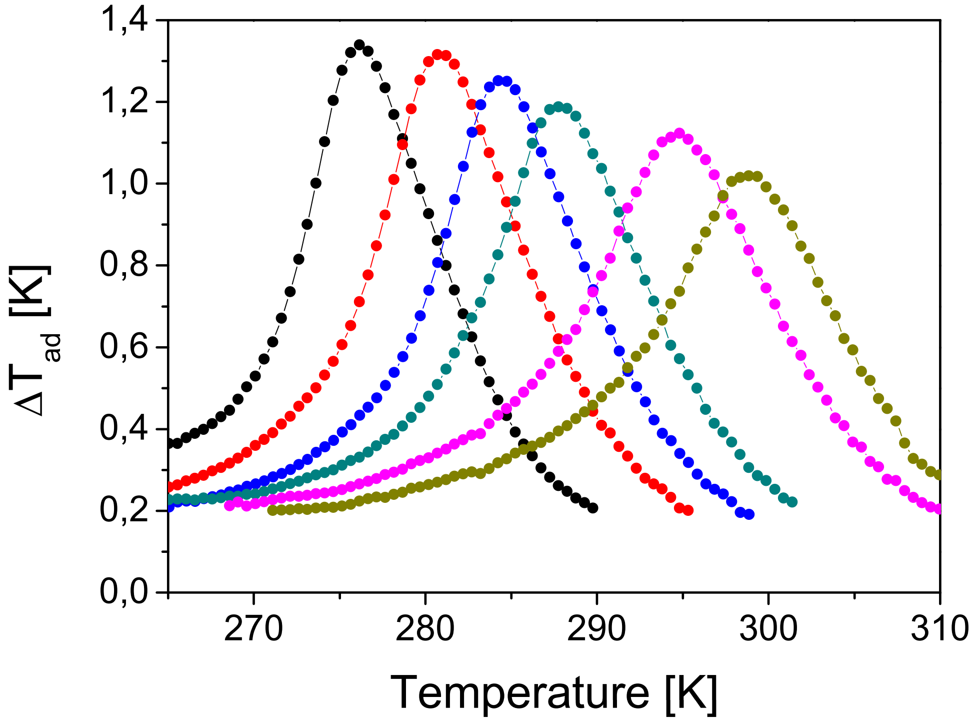
Perovskite manganites

- A series of manganites has been prepared, varying Ca/Sr.
- The Curie temperature can be controlled.
- ΔT_{ad} is the temperature change of the material when 1 T magnetic field is applied.
- It is measured directly



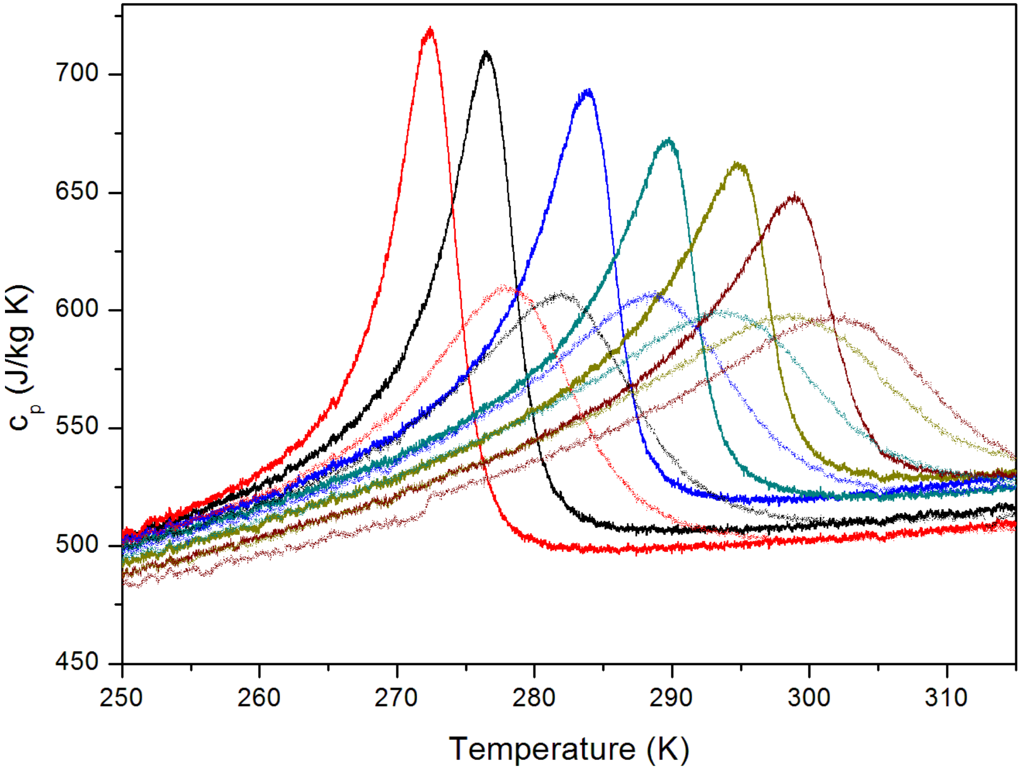
$La_{0.67}Ca_{0.33-x}Sr_xMn_{1.05}O_3$

$x = 0.04 - 0.09$



Specific heat of the perovskites

- Full lines are 0 T and dotted are 1 T magnetic field

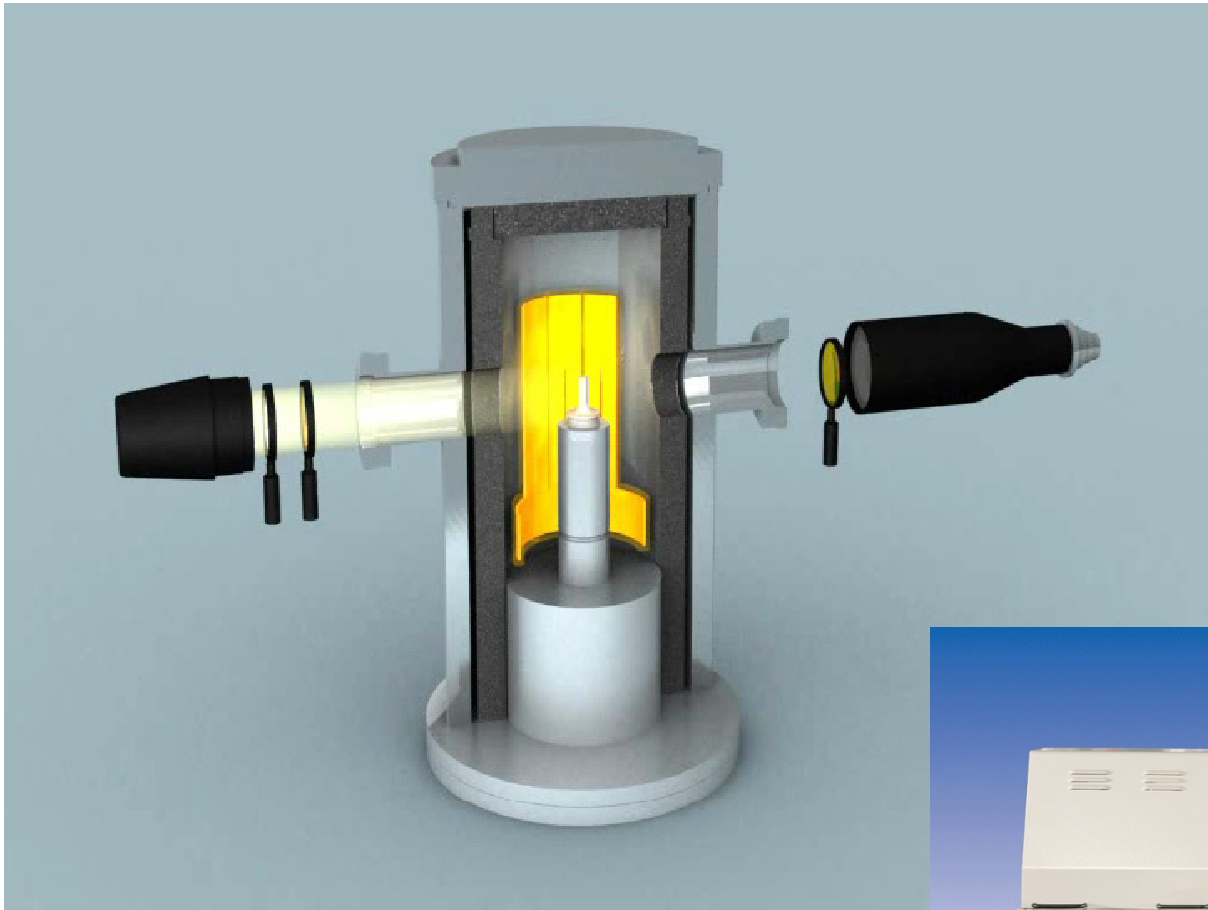


- The adiabatic temperature change (ΔT_{ad}) can be found directly or by measuring magnetisation *(m)* and specific heat (c_p) versus temperature (*T*) and magnetic field (*H*).

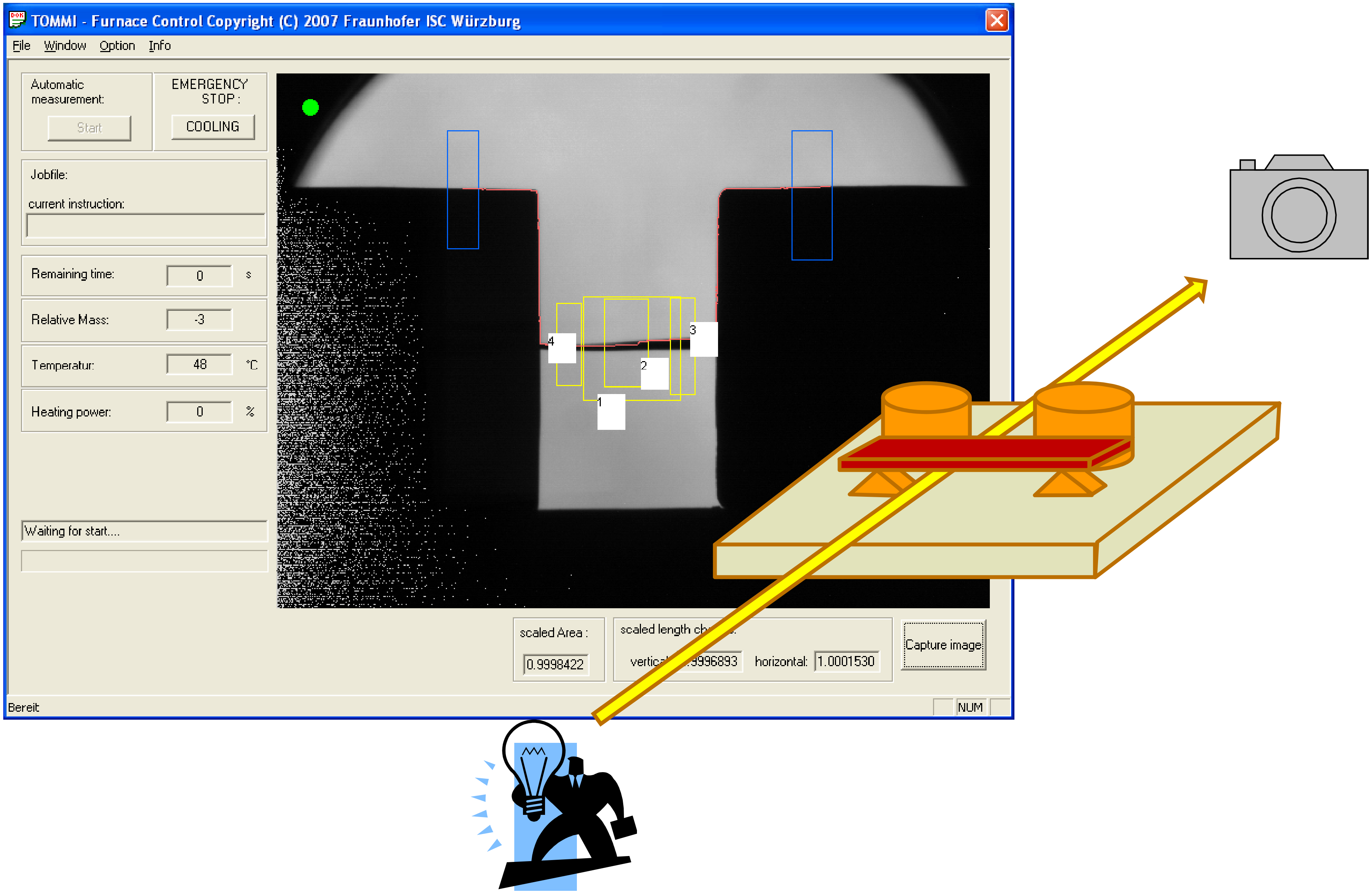
$$\Delta T_{\mathrm{ad}} = -\mu_0 \int_{H_{\mathrm{i}}}^{H_{\mathrm{f}}} \frac{T}{c_{\mathrm{p}}} \left(\frac{\partial m}{\partial T}\right)_H dH$$

Bjørk *et al.* J. Magn. Mater. **322**, 3882 (2010)

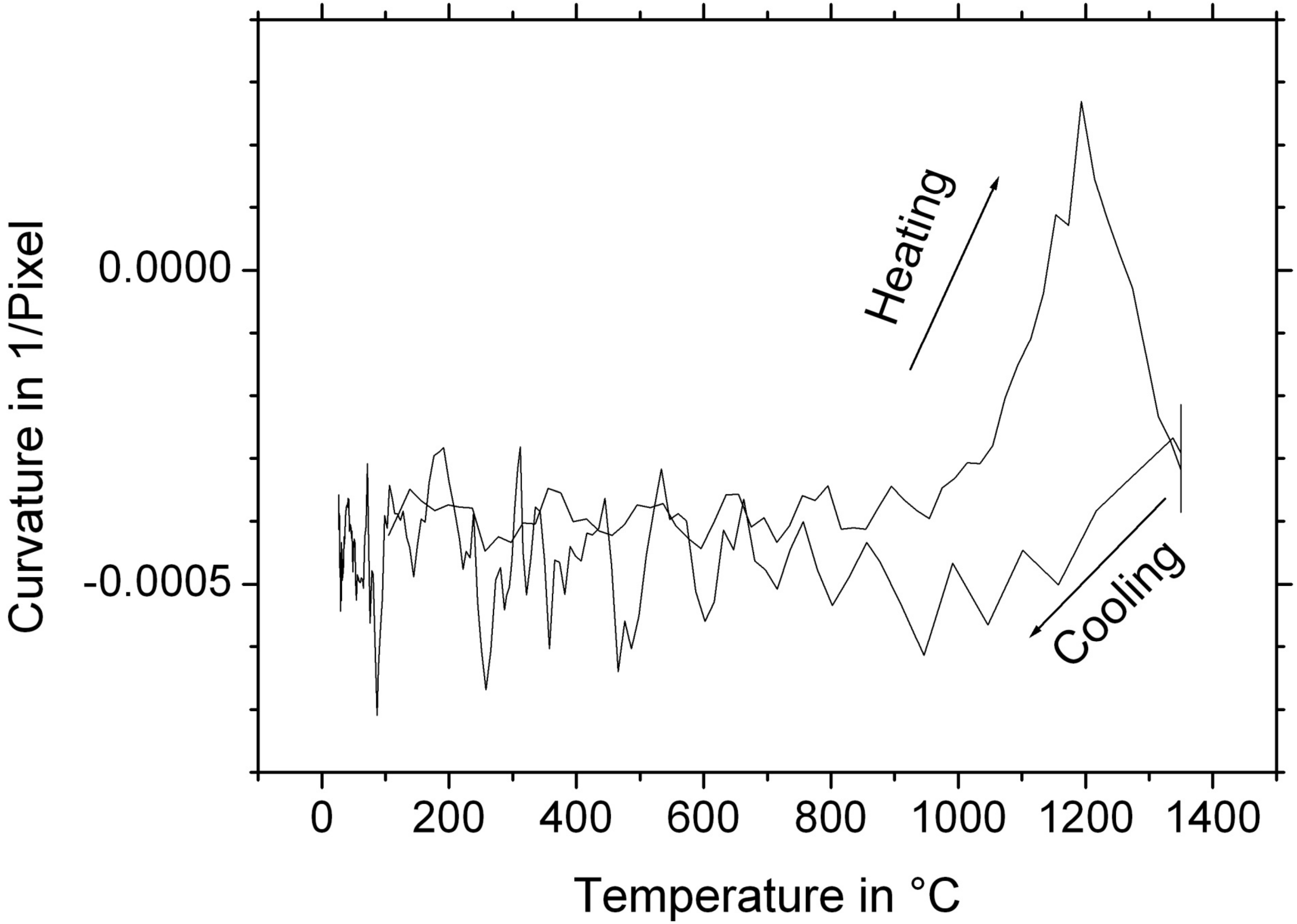
Optical dilatometer



Analysis set-up

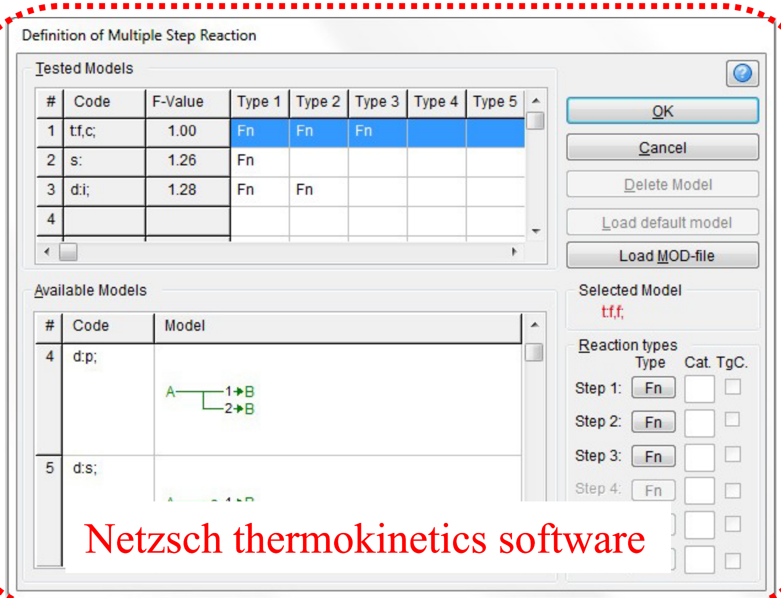


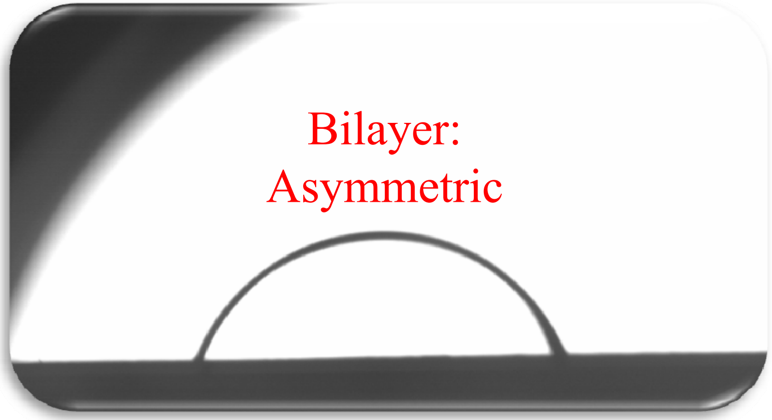
Bending during sintering a fuel cell



Optimization of a binder removal profile

The aim is to optimize binder removal- and sintering profiles in order to reduce warping of LSM/CGO bilayers.
Processes are characterised through analysis of the kinetic field.

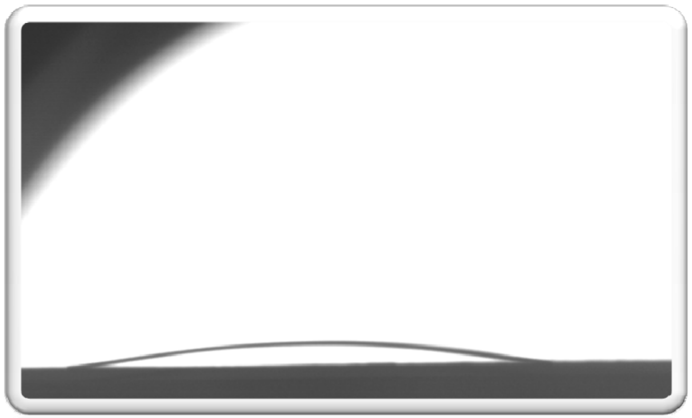




166°C

?

Improve the shape stability

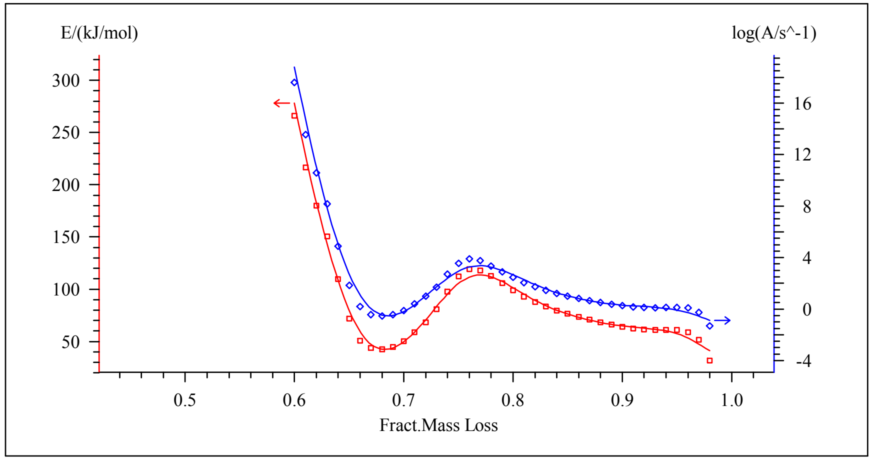


Contact: DeWei Ni, dwei@dtu.dk

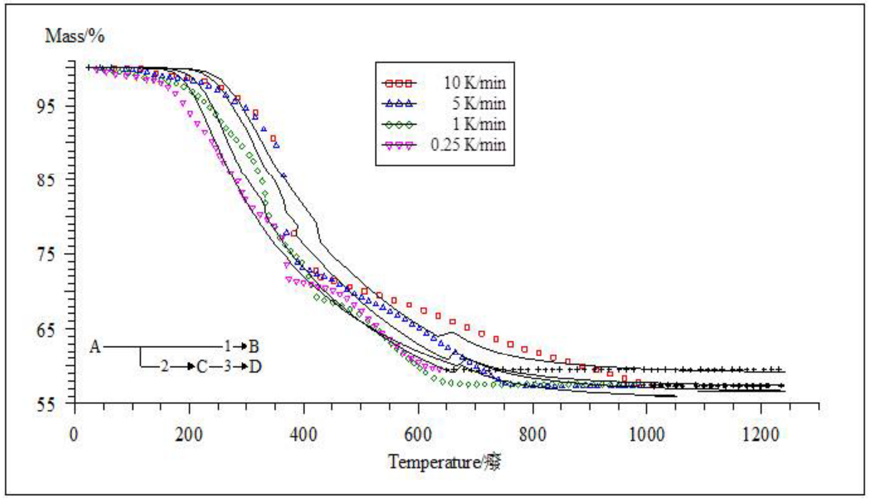
Binder removal thermokinetics analysis

CGO Tapes:

Friedman Analysis CGO

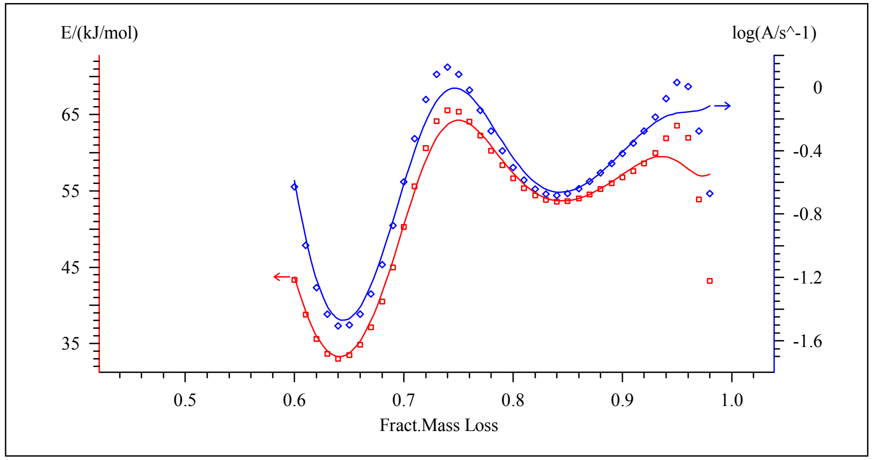


NETZSCH Thermokinetics CGO

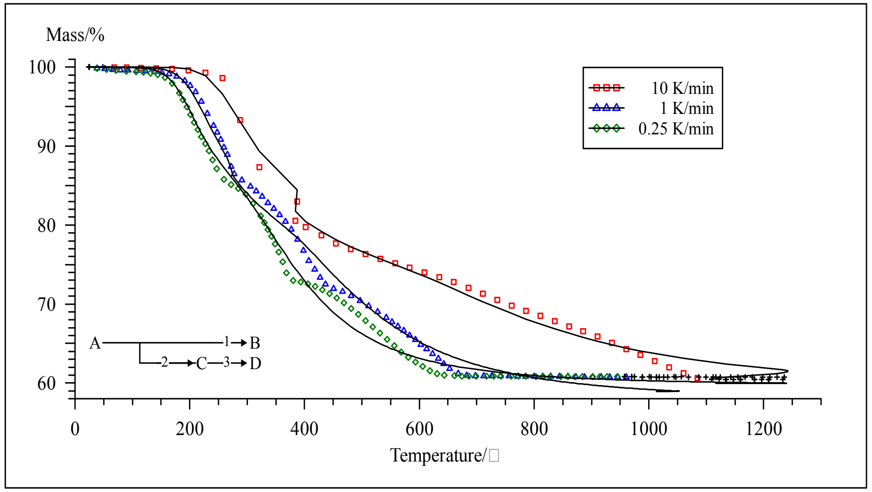


LSM/CGO Bilayer tapes:

Friedman Analysis LSM/CGO

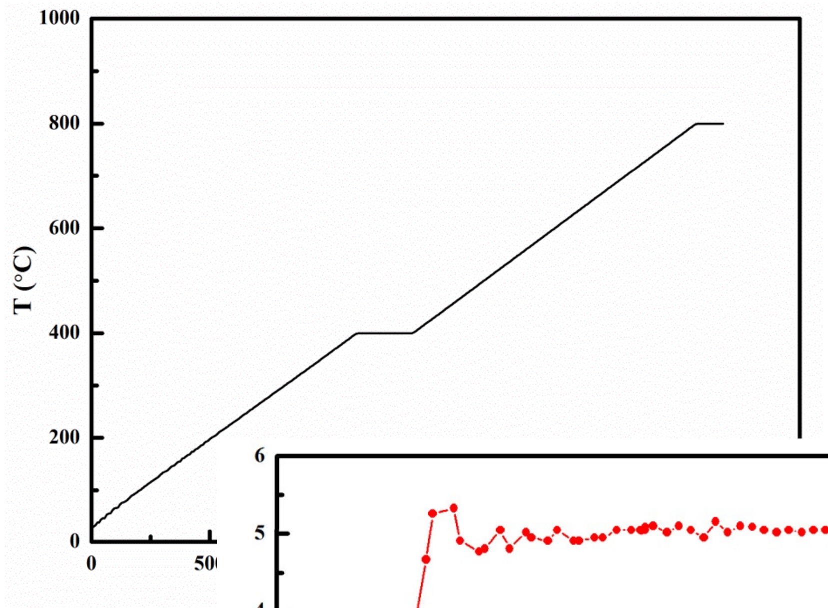


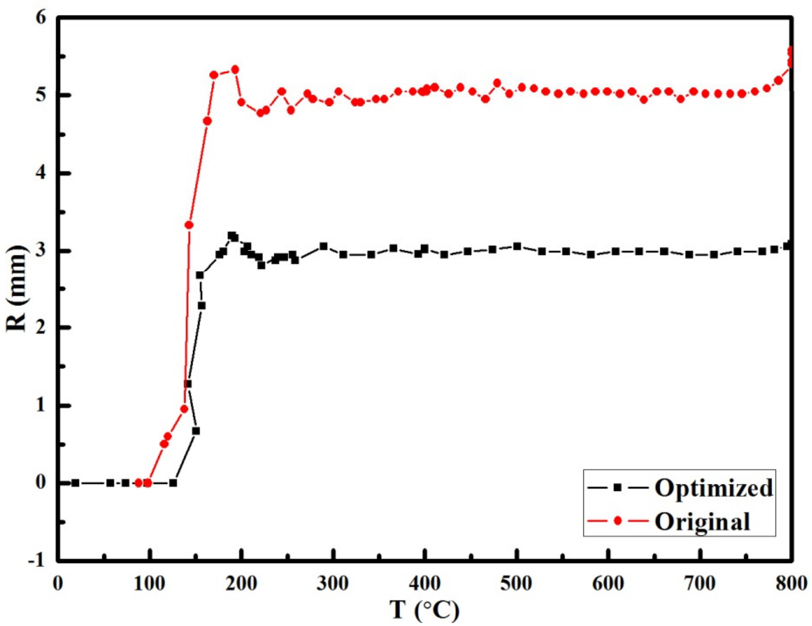
NETZSCH Thermokinetics LSM/CGO



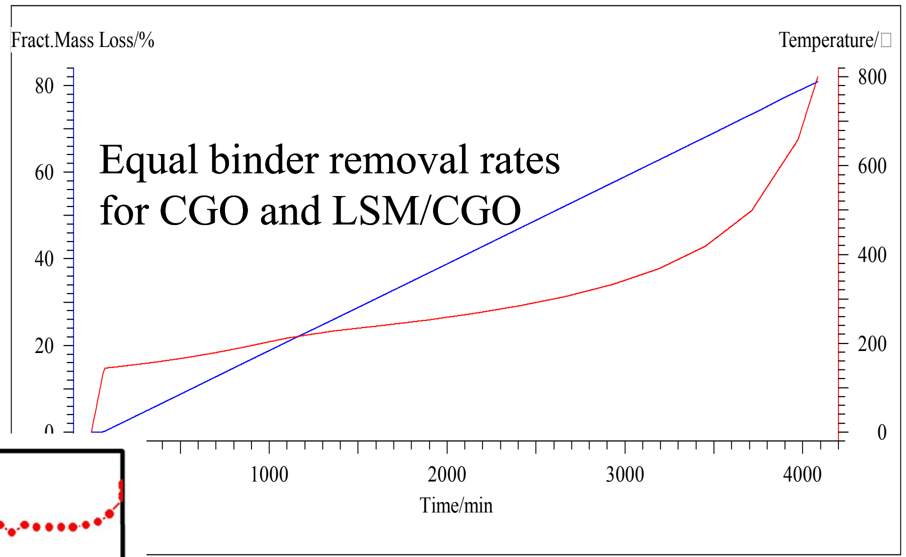
Binder removal profile improved

Original profile





Optimized profile



Original

Optimized

Sintering of CGO, $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$

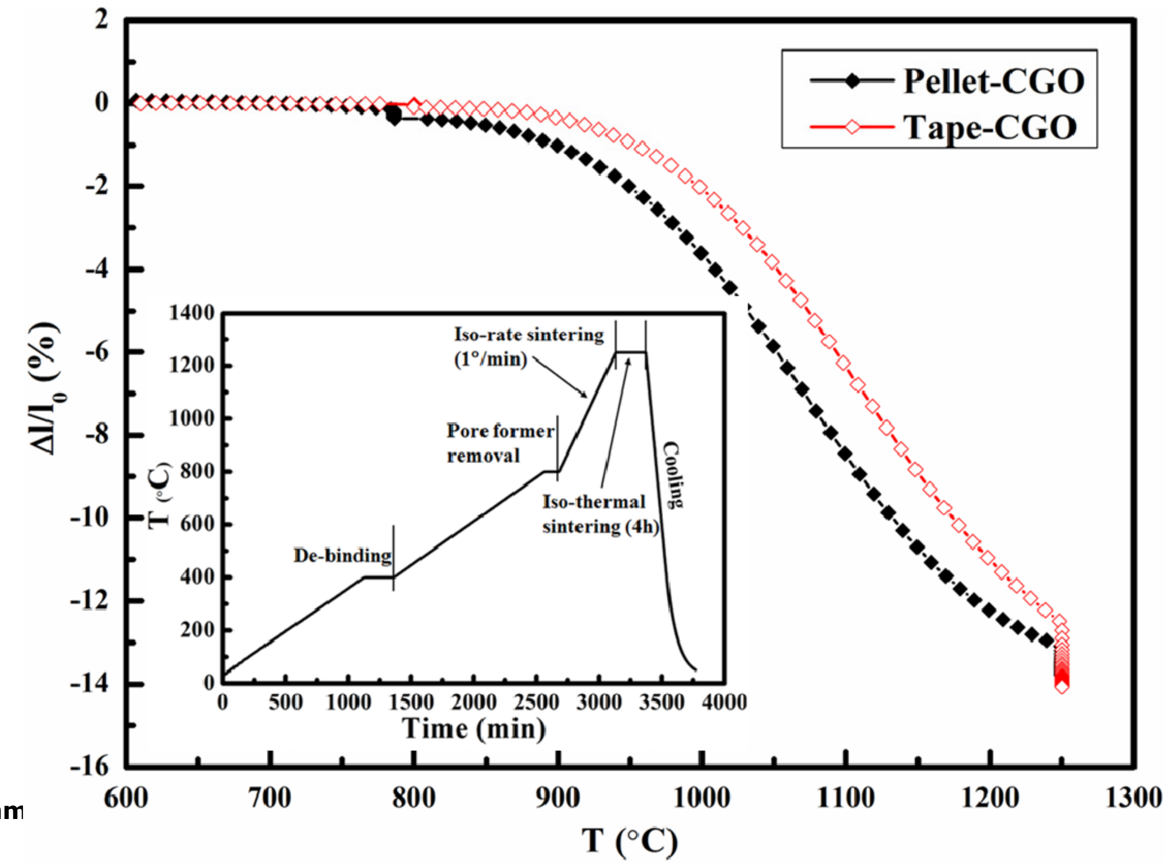
Scope is to study the densification behaviour of powder from two different processing methods – tape casting and dry pressing – as well as addition of sintering aids to control sintering behaviour:

For the same composition, the densification behaviour is different between dry pressing pellets and tape casting layers.

Green density:

Tape cast: ~40%TD

Dry pressed: ~50%TD



Densification, analysis of kinetics

Theoretical approach:

I. Iso-conversion lines:

$$\dot{\rho} = \frac{A}{RT}\exp(\frac{-Q_d}{RT})f(\rho,d) \qquad \ln(\dot{\rho}T) = \frac{-Q_d}{RT} + \ln\frac{A}{R} + \ln f(\rho,d)$$

$$\ln(-\frac{dl}{dt}T) = \frac{-Q_l}{RT} + \ln\frac{C}{R} + \ln f(l,d)$$

II. Master Sintering Curve (MSC):

$$\frac{d\rho}{3\rho dt} = \frac{\gamma\Omega(\Gamma(\rho))D_0}{kT(G(\rho))^n}\exp(-\frac{Q}{RT}) \qquad \Theta(t,T(t)) \equiv \int_0^t \frac{1}{T}\exp(-\frac{Q}{RT})dt$$

Sintering at different heating rates

$\downarrow$

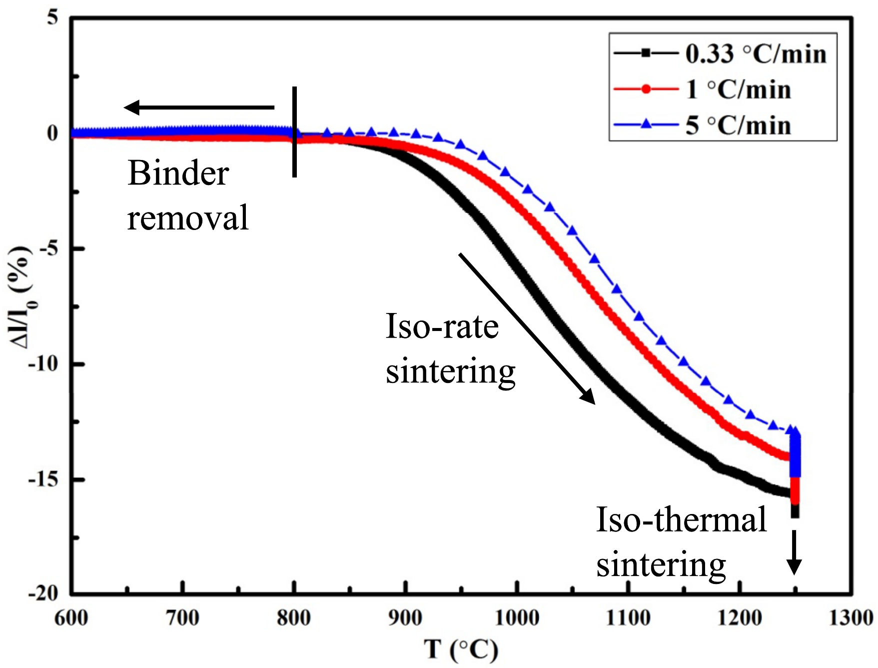
Activation energy (Q)

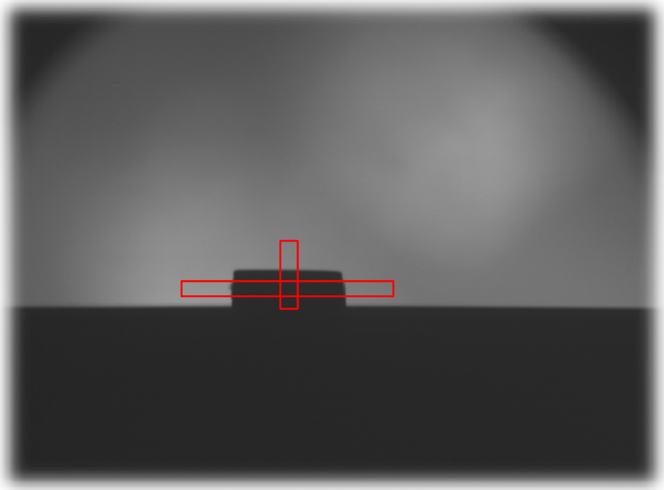
III. Dorn's method

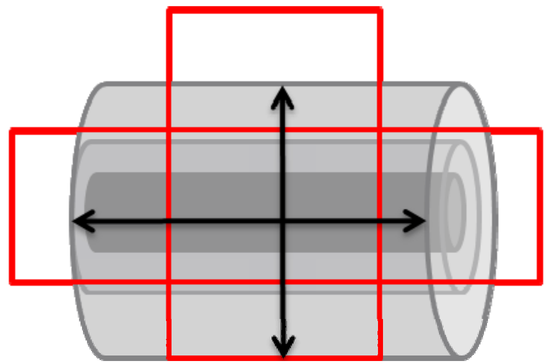
Step-wise isothermal heating

Densification at different heating rates

Shrinkage of CGO-tape

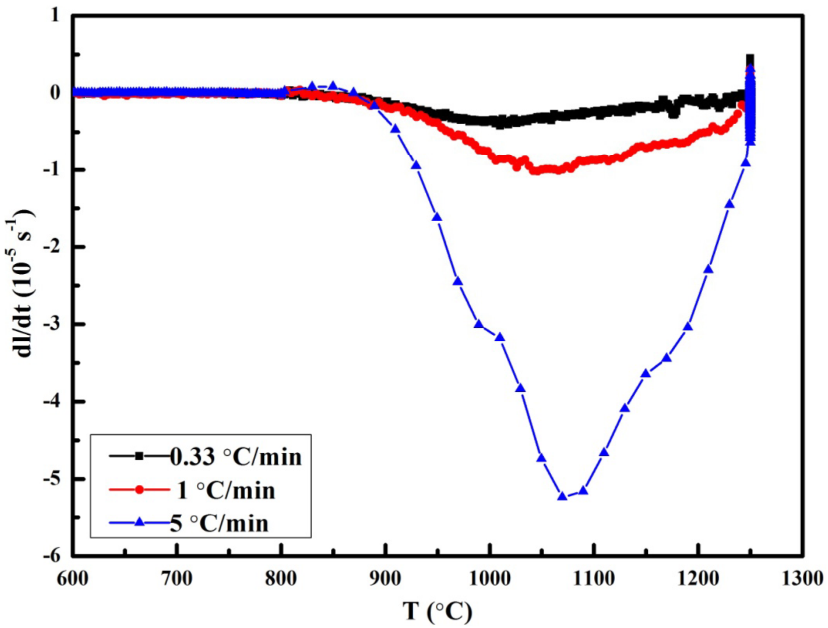




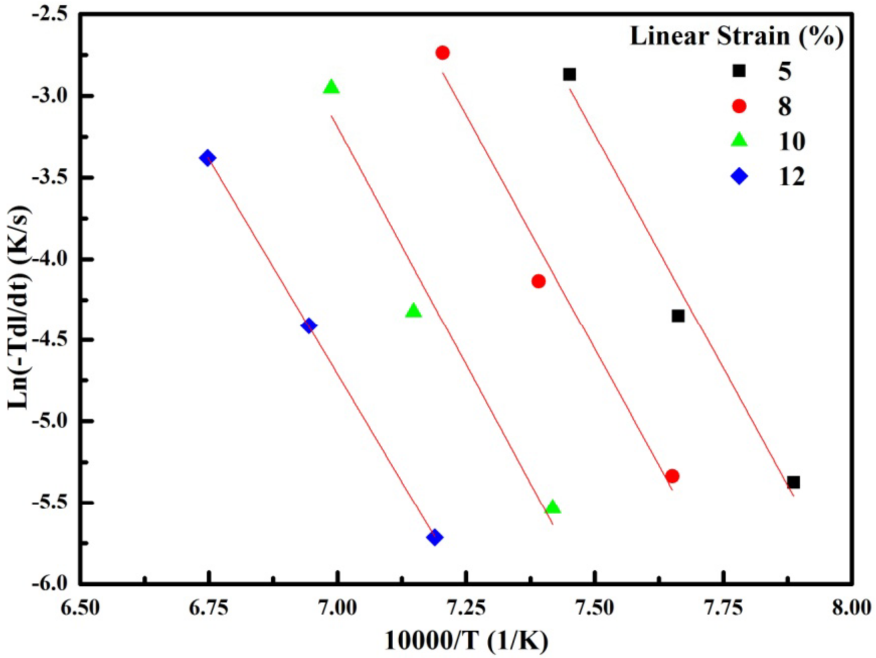


Activation energy

Determined by iso-conversion lines (sintering strain)



$$\ln\left(-\frac{dl}{dt}T\right)=\frac{-Q_l}{RT}+\ln\frac{C}{R}+\ln f(l,d)$$



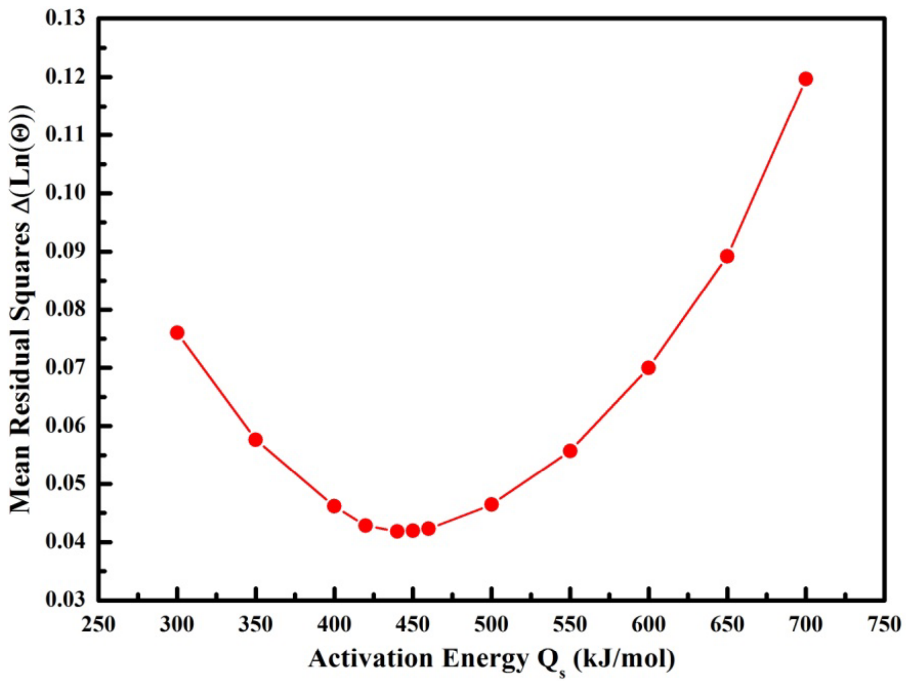
E_{CGO}=440~485 kJ/mol

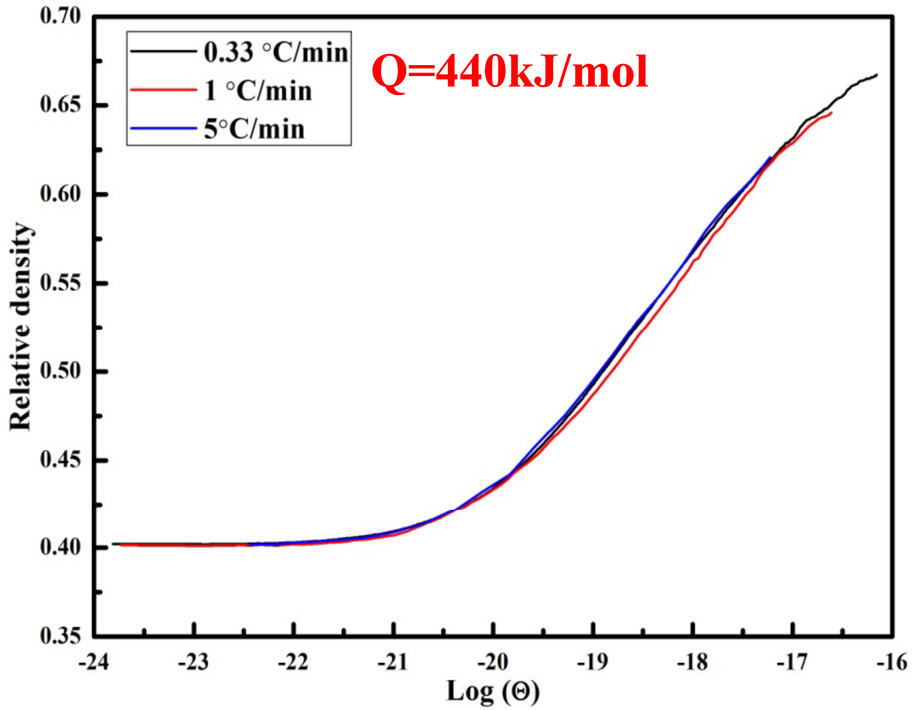
Activation energy determined by MSC

Mean Residual Squares:

$$MRS = \sqrt{\frac{1}{\rho_f - \rho_0} \int_{\rho_0}^{\rho_f} \frac{\sum_{i=1}^{N} \left(\left(\Theta_i / \Theta_{avg} \right) - 1 \right)^2}{N} d\rho}$$

$$\Theta(t, T(t)) \equiv \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt$$

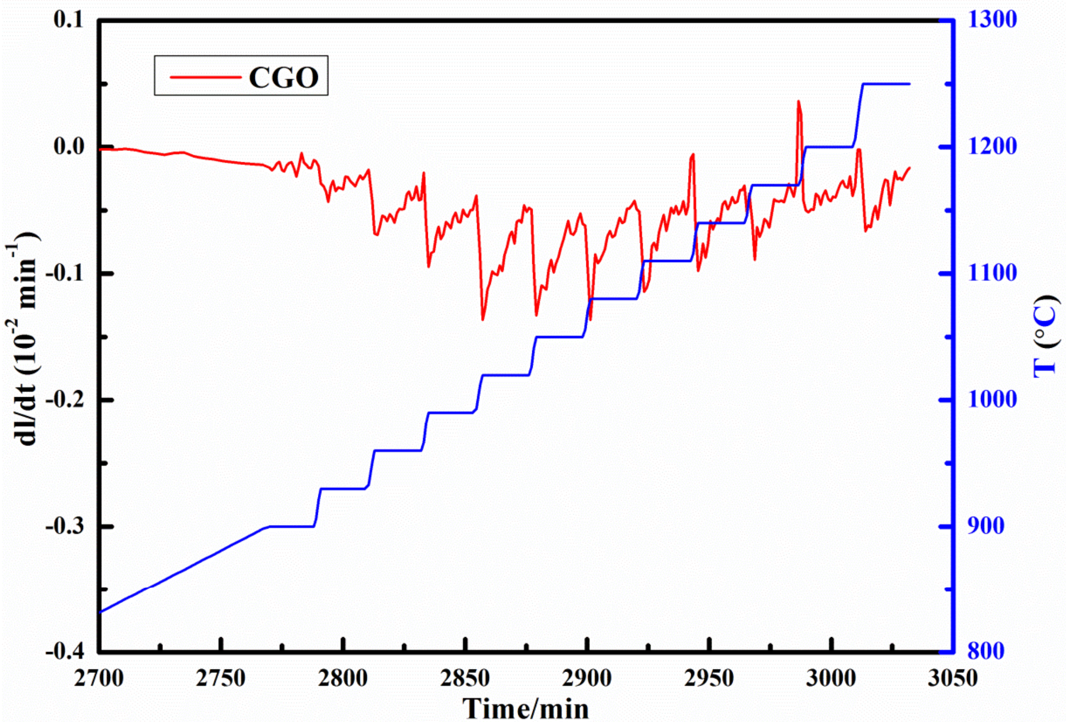




Activation energy determined by Dorn's method:

$$v = \frac{d\left(\Delta l / l_0\right)}{dt} = k(T)\frac{\left(\Delta l / l_0\right)^{1-n}}{n}$$

$$Q = \frac{RT_1T_2}{T_2 - T_1}\ln\left(\frac{T_2 v_2}{T_1 v_1}\right)$$



Activation energy (kJ/mol):

T(°C)	930	960	990	1020	1050	1080	1110
CGO	422	459	471	468	499	417	451

Activation energy via different methods

Iso-conversion lines method:

Shrinkage (%)	5	8	10	12
CGO (kJ/mol)	478	477	486	439

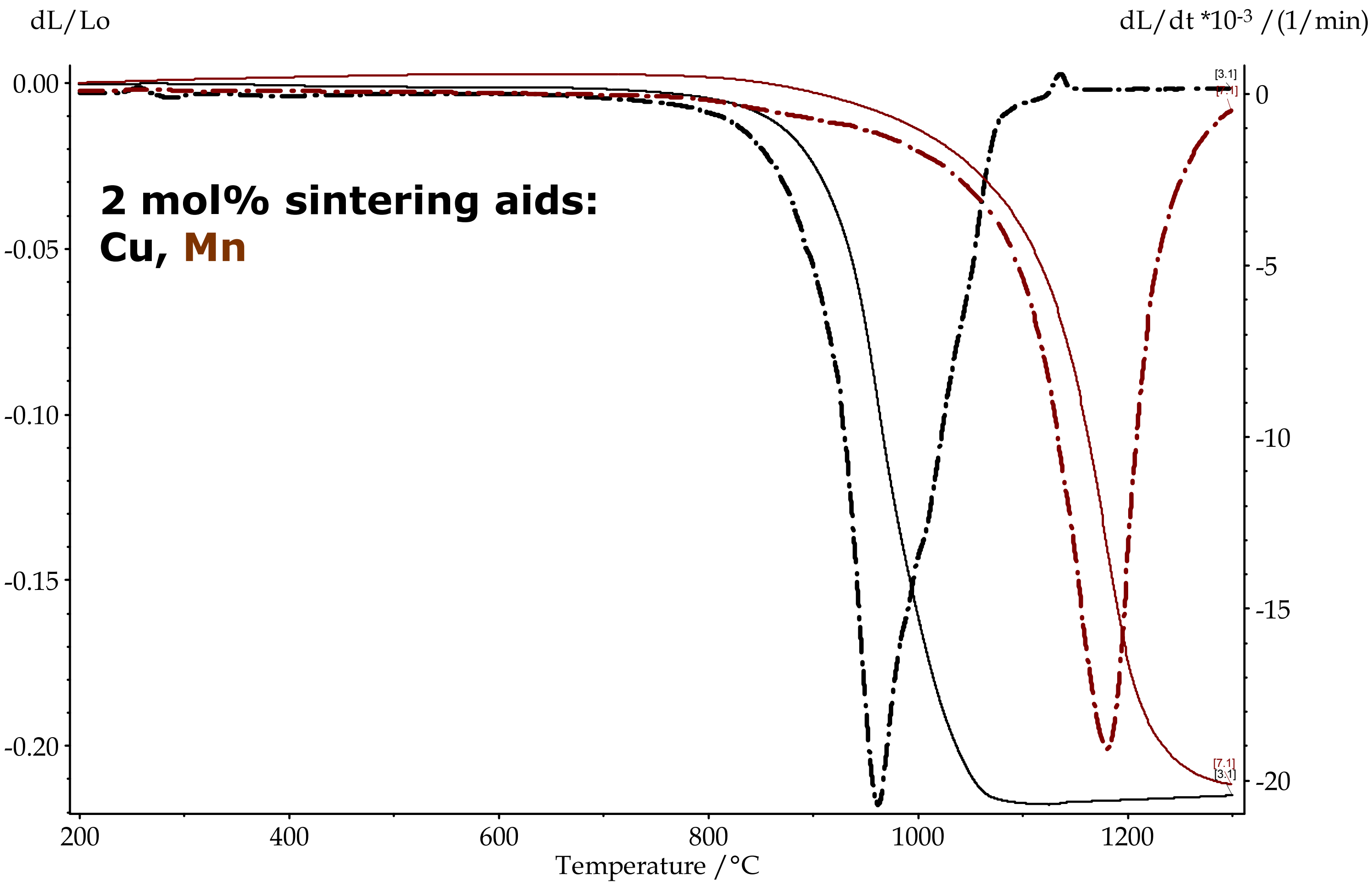
Master sintering curve:

Relative density	Full range
CGO (kJ/mol)	440

Dorn's method:

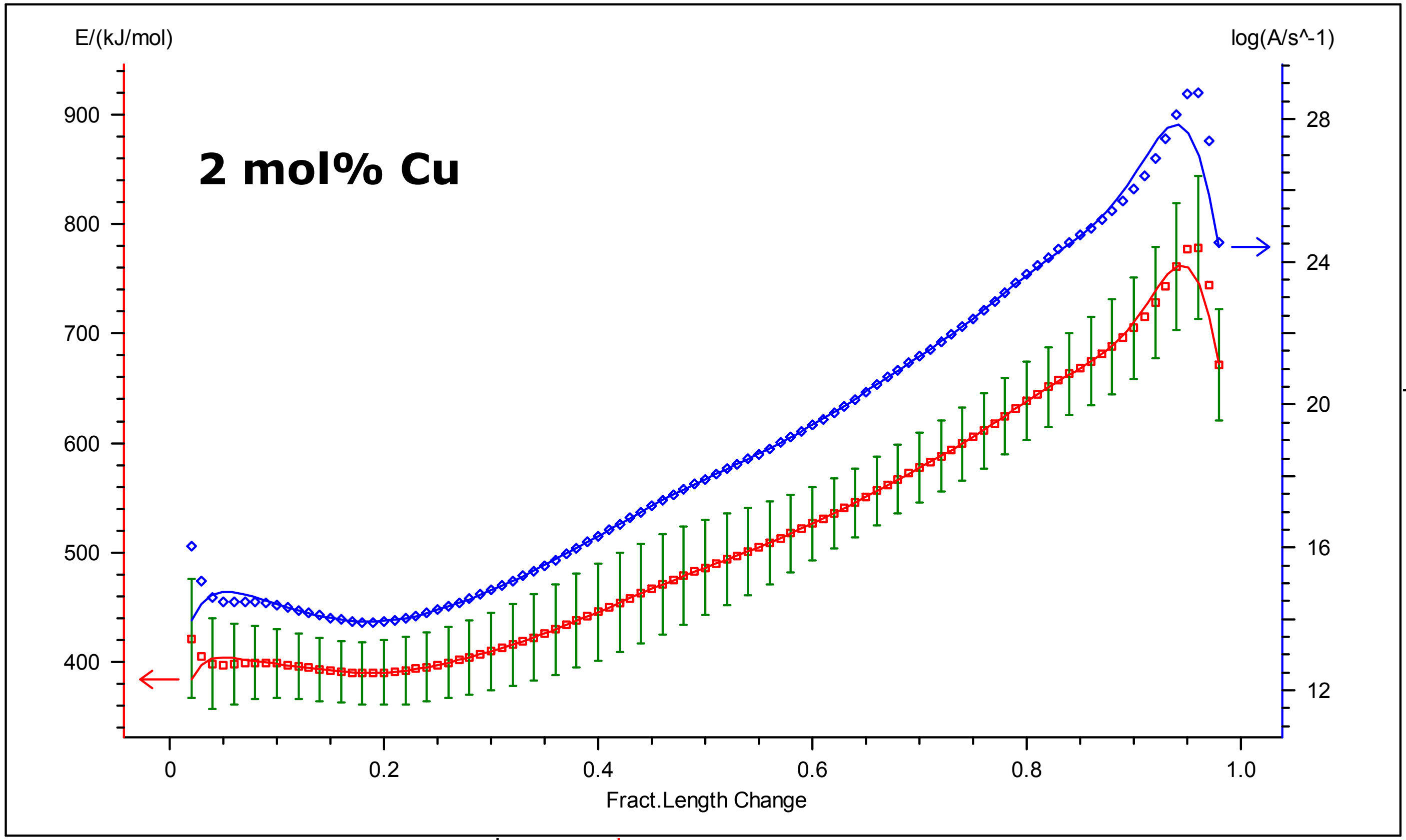
T(°C)	930	960	990	1020	1050	1080	1110
CGO (kJ/mol)	422	459	471	468	499	417	451

Sintering aids to control shrinkage

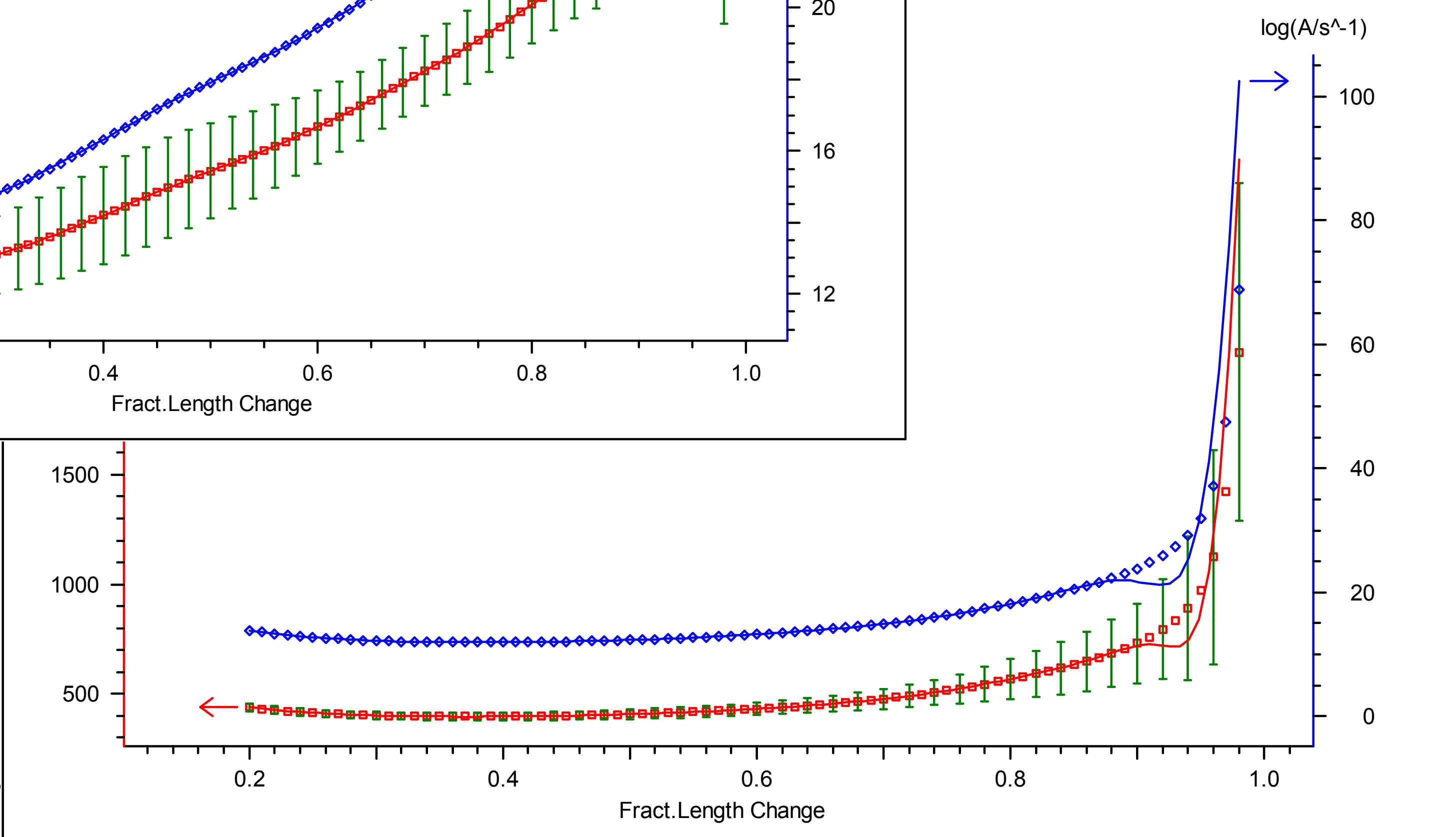


Activation energy by iso-conversion lines

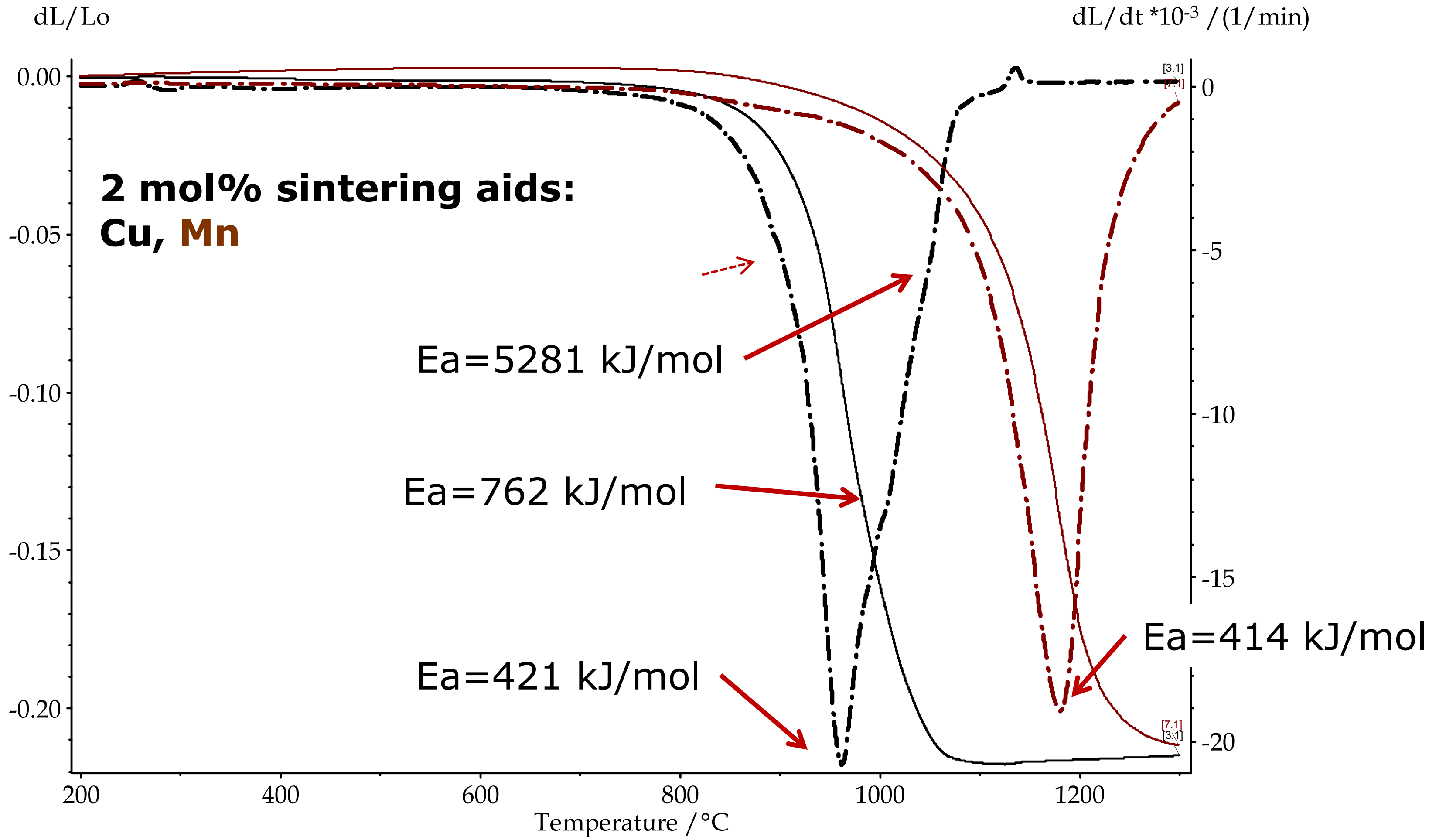
Friedman Analysis



2 mol% Mn



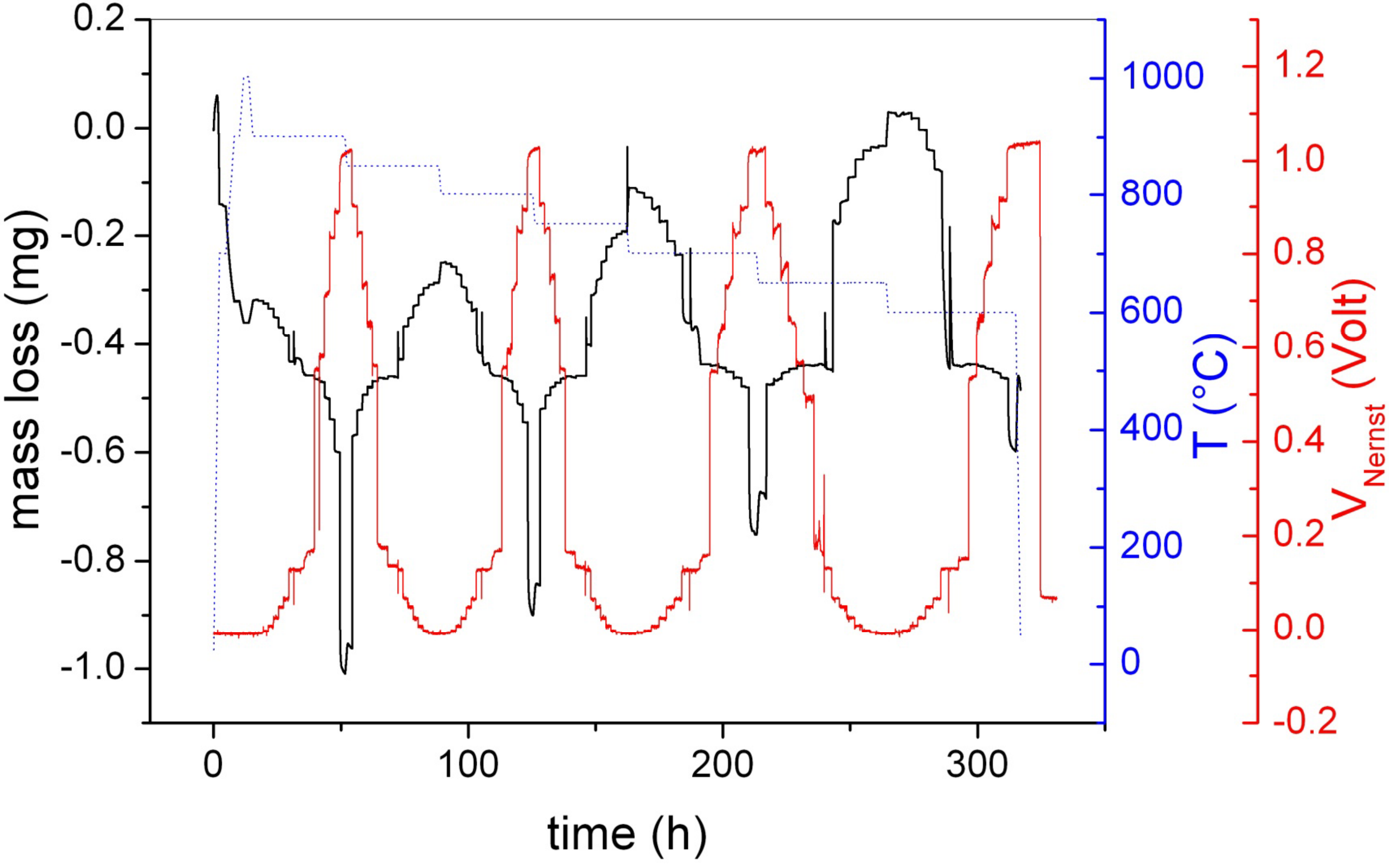
Activation energy for CGO with sintering aids



CGO (pure): Ea~480 kJ/mol

Studying gas-solid reactions

The symmetrical furnace design of the TG439 facilitates the running of longer and complicated heating- and gas-profiles, as it is not necessary to run a baseline.
The sample sizes are small and the balance sensitivity high, hence perfect for studying gas-solid reactions.

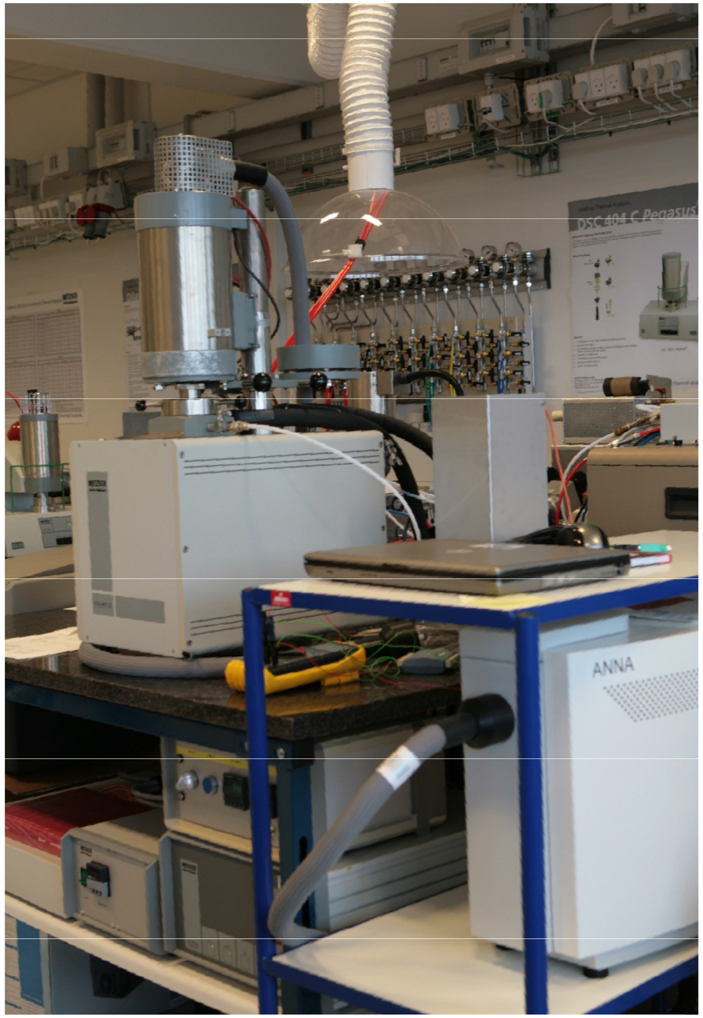


Weight change of $Ce_{0.8}Pr_{0.2}O_{2-\delta}$ as a function of T, $P_{O2}(V_{Nernst})$

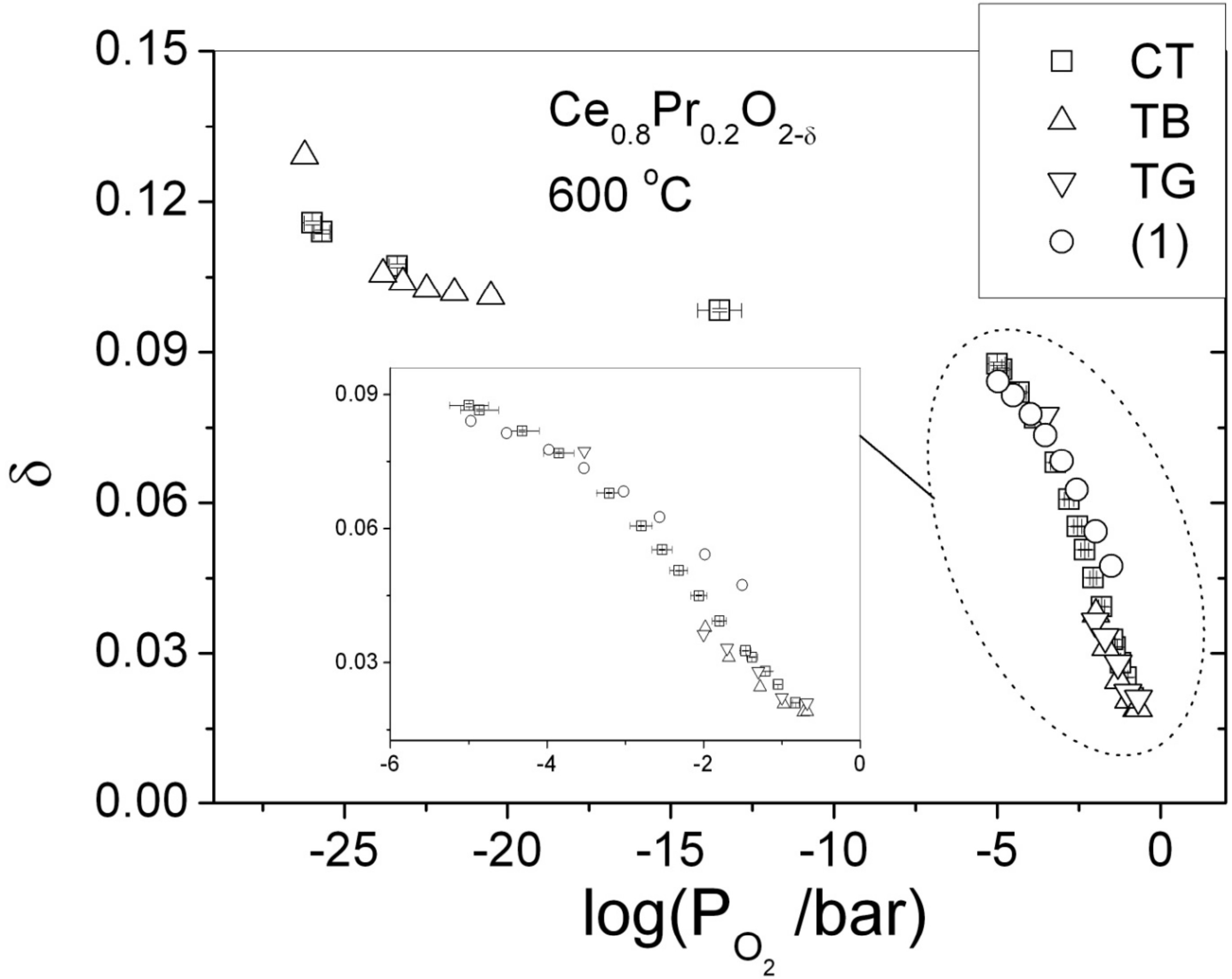
 Contact: Christos Chatzichristodoulou, ccha@dtu.dk

Netzsch TG439

Netzsch STA 409CD

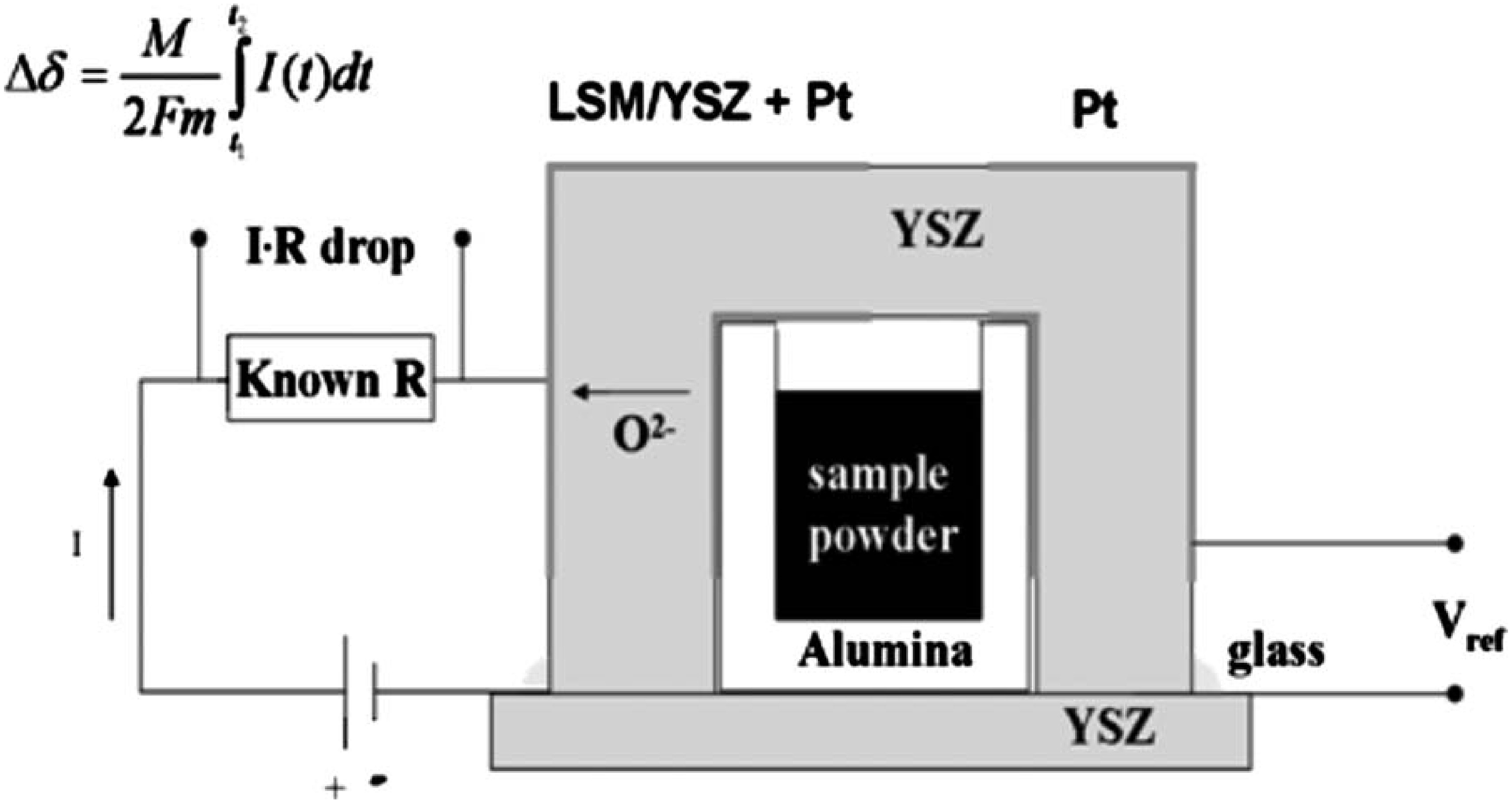


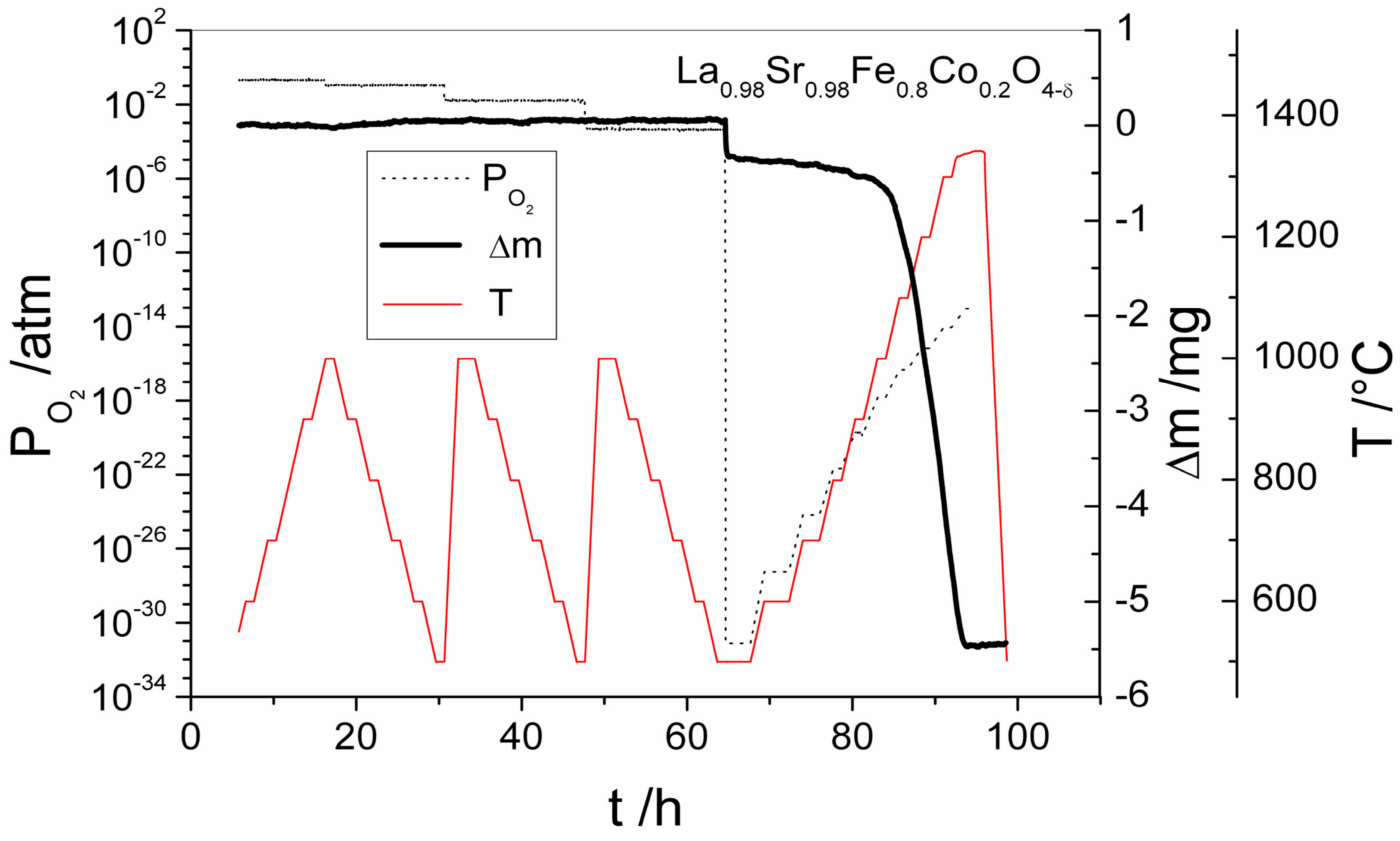
Oxygen nonstoichiometry – $Ce_{0.8}Pr_{0.2}O_{2-\delta}$ (CPO20)



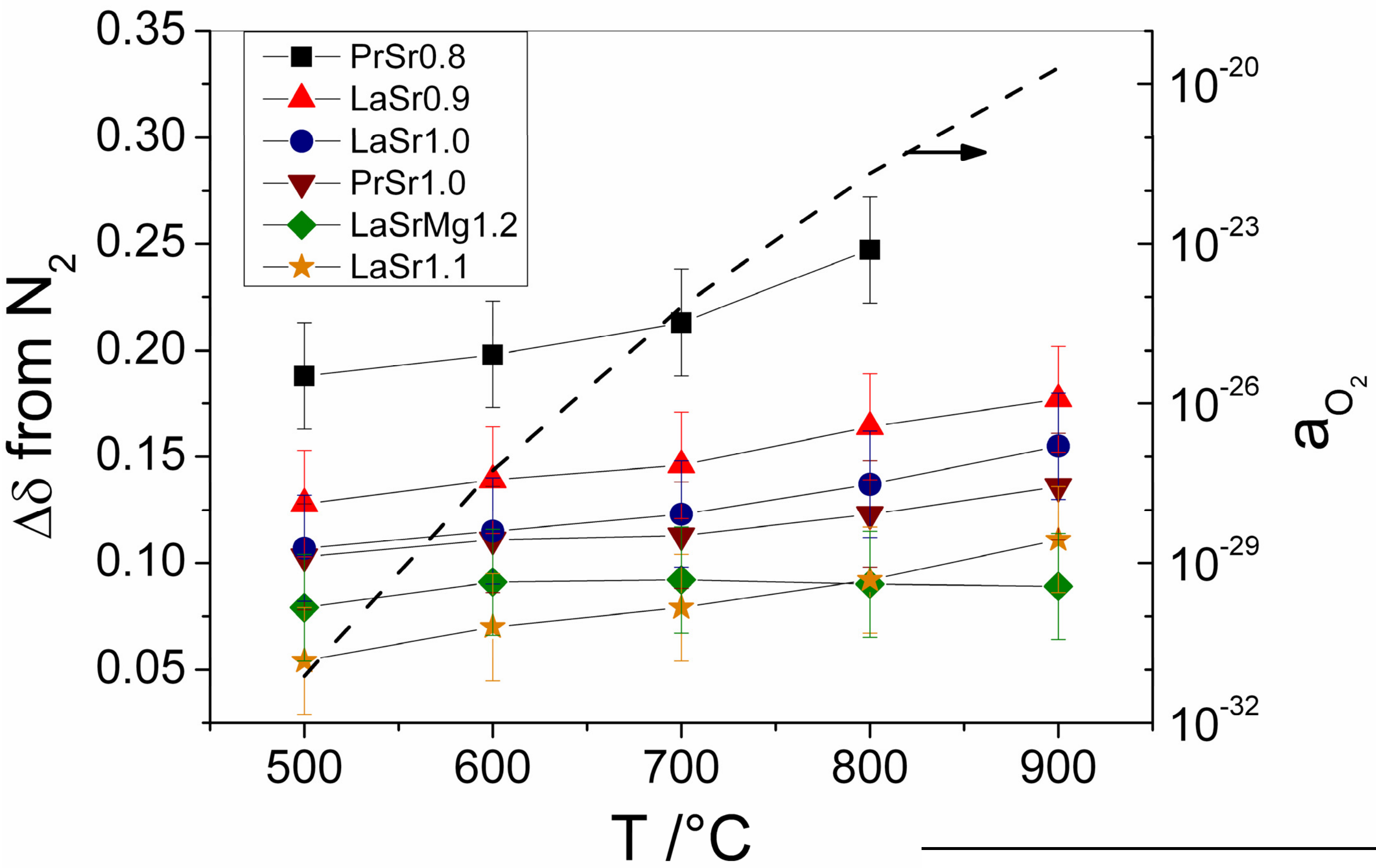
(1) T. S. Stefanik and H. L. Tuller, *J. Electroceram.*, **13**, 799 (2004).

Experimental setup used for coulometric titration





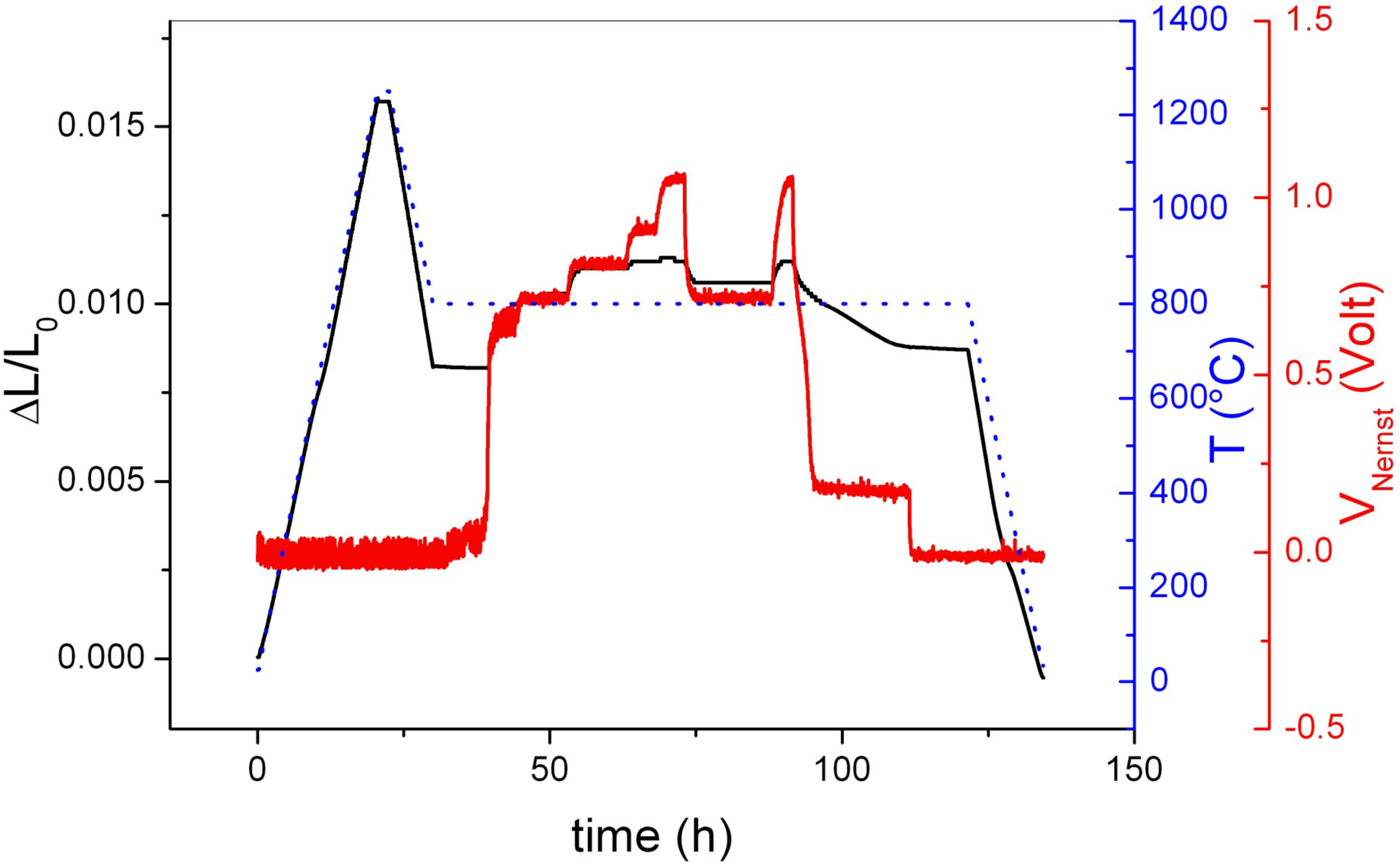
35 Weight change of $La_{0.98}Sr_{0.98}Fe_{0.8}Co_{0.2}O_{4-\delta}$ as a function of T, $P_{O2}(V_{Nernst})$



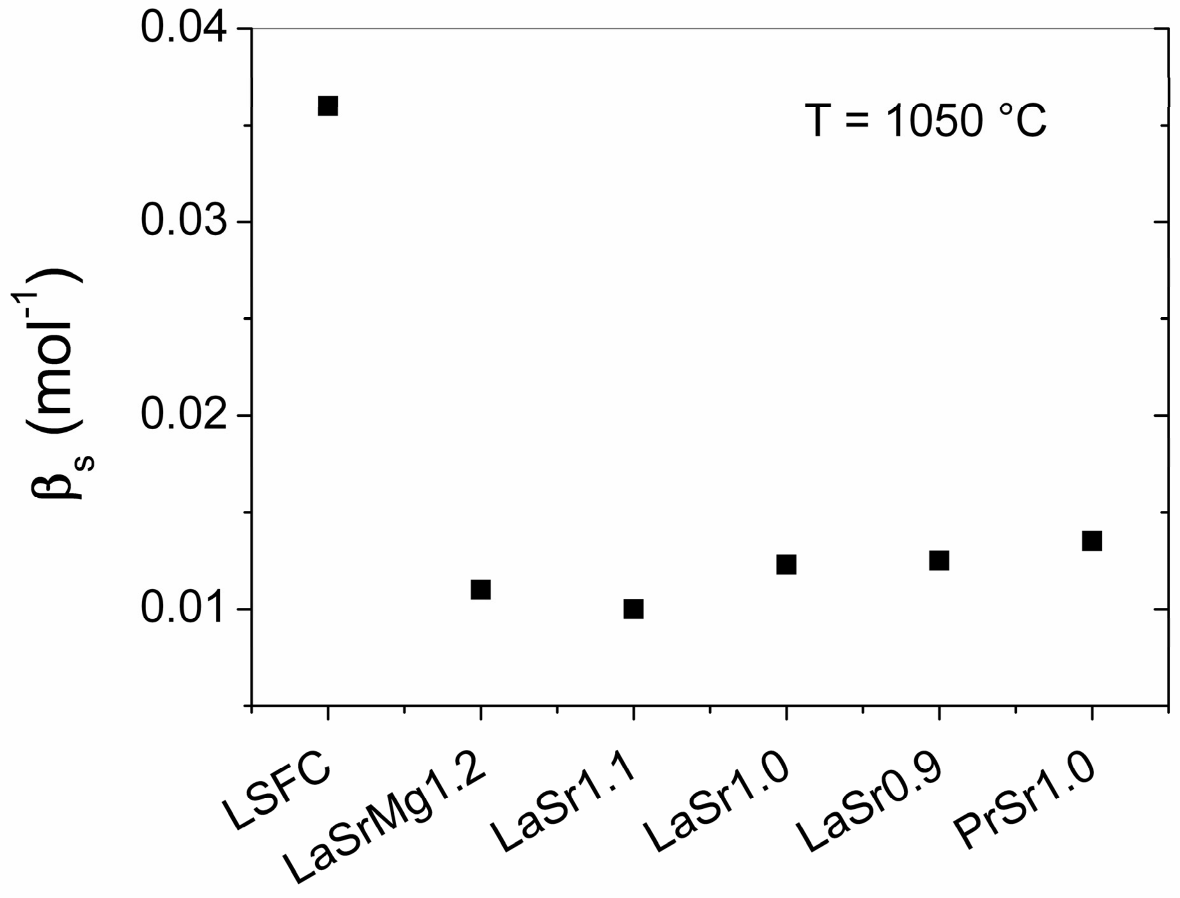
Composition	Abbreviated Name
$La_{1.08}Sr_{0.88}Fe_{0.8}Co_{0.2}O_{4-\delta}$	LaSr1.1
$La_{0.98}Sr_{0.98}Fe_{0.8}Co_{0.2}O_{4-\delta}$	LaSr1.0
$La_{0.88}Sr_{1.08}Fe_{0.8}Co_{0.2}O_{4-\delta}$	LaSr0.9
$Pr_{0.98}Sr_{0.98}Fe_{0.8}Co_{0.2}O_{4-\delta}$	PrSr1.0
$Pr_{0.78}Sr_{1.18}Fe_{0.8}Co_{0.2}O_{4-\delta}$	PrSr0.8
$La_{1.18}Sr_{0.78}Fe_{0.64}Co_{0.16}Mg_{0.2}O_{4-\delta}$	LaSrMg1.2

Temperature dependence of the oxygen nonstoichiometry of Ruddlesden-Popper samples in H_2/H_2O=50 relative to their oxygen nonstoichiometry in N_2, estimated by thermo-gravimetry. The P_{O2} profile is also shown as a function of temperature.

Dilatometry in a DIL 402CD

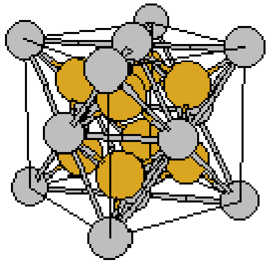


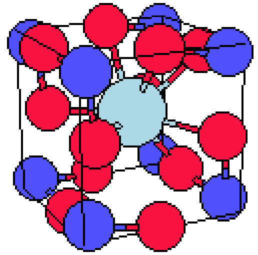
Length change of $La_{0.98}Sr_{0.98}Fe_{0.8}Co_{0.2}O_{4-\delta}$ as a function of T, $P_{O2}(V_{Nernst})$

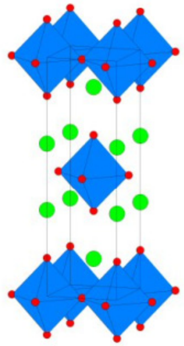


Chemical expansion coefficient of the various single phase Ruddlesden-Popper compositions measured at 1050 ^{o}C using air/CO_2/H_2 mixtures. The corresponding value of the perovskite $(La_{0.6}Sr_{0.4})_{0.99}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (LSFC) measured at 800 ^{o} C using air/CO_2 mixtures is also shown for comparison.

Materials







Flourite structure

Perovskite structure

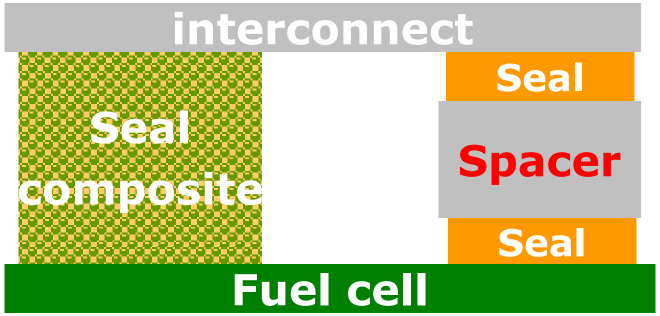
Ruddlesden-Popper structure

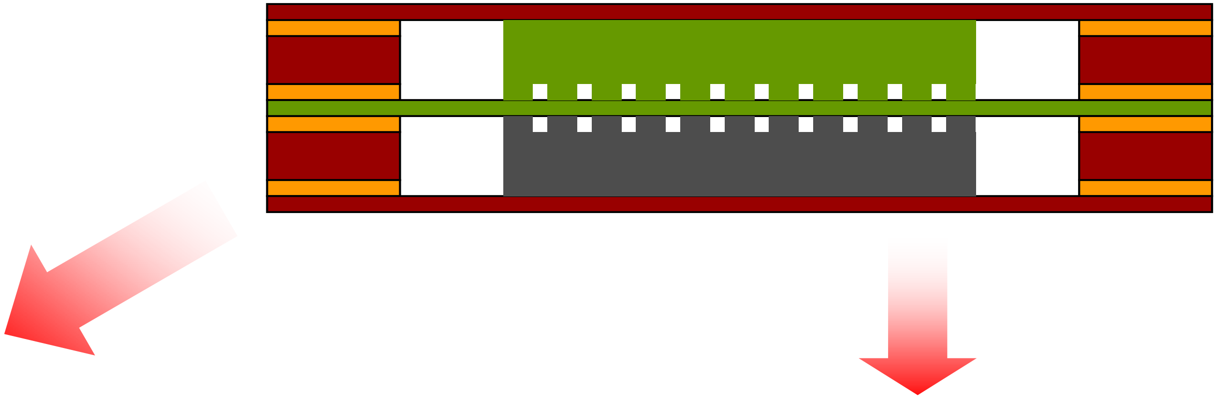
Depending on the specific application different structure types can be utilized

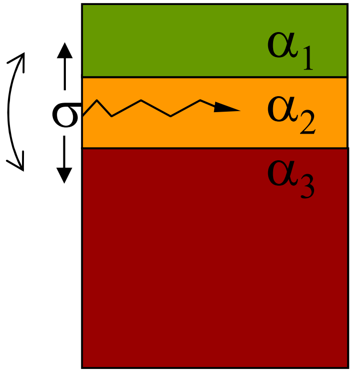
Oxide ion conductivity

Dimensional stability

Seal design and thermally induced stresses



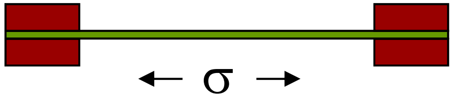




$\alpha_2 < \alpha_1 , \alpha_3$

Seal Edge Fracture

Assembly Stress



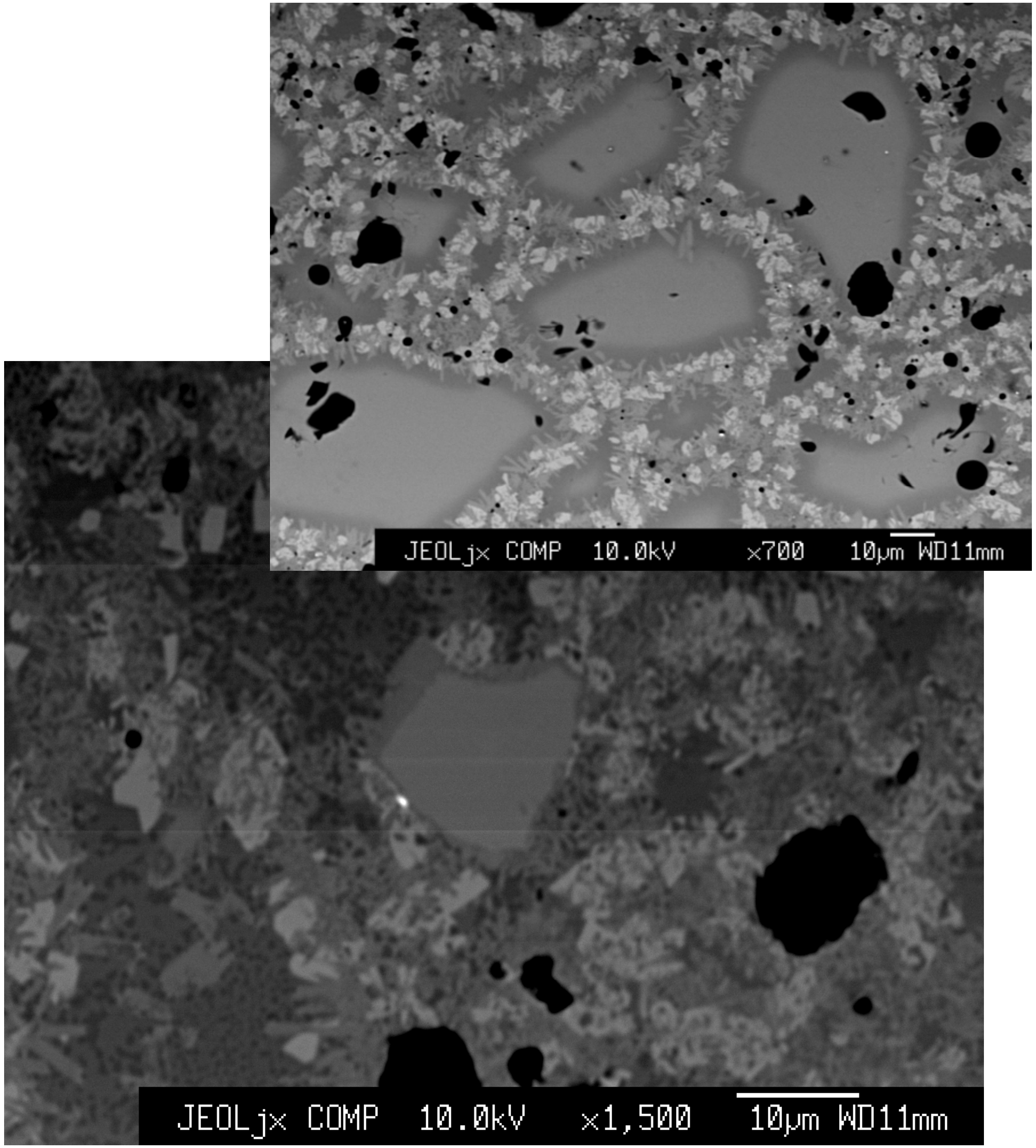
Soda lime magnesia aluminoborosilicate glass

Addition of a filler material with high CTE increases CTE of the crystallized glass. Filler and glass may behave independently

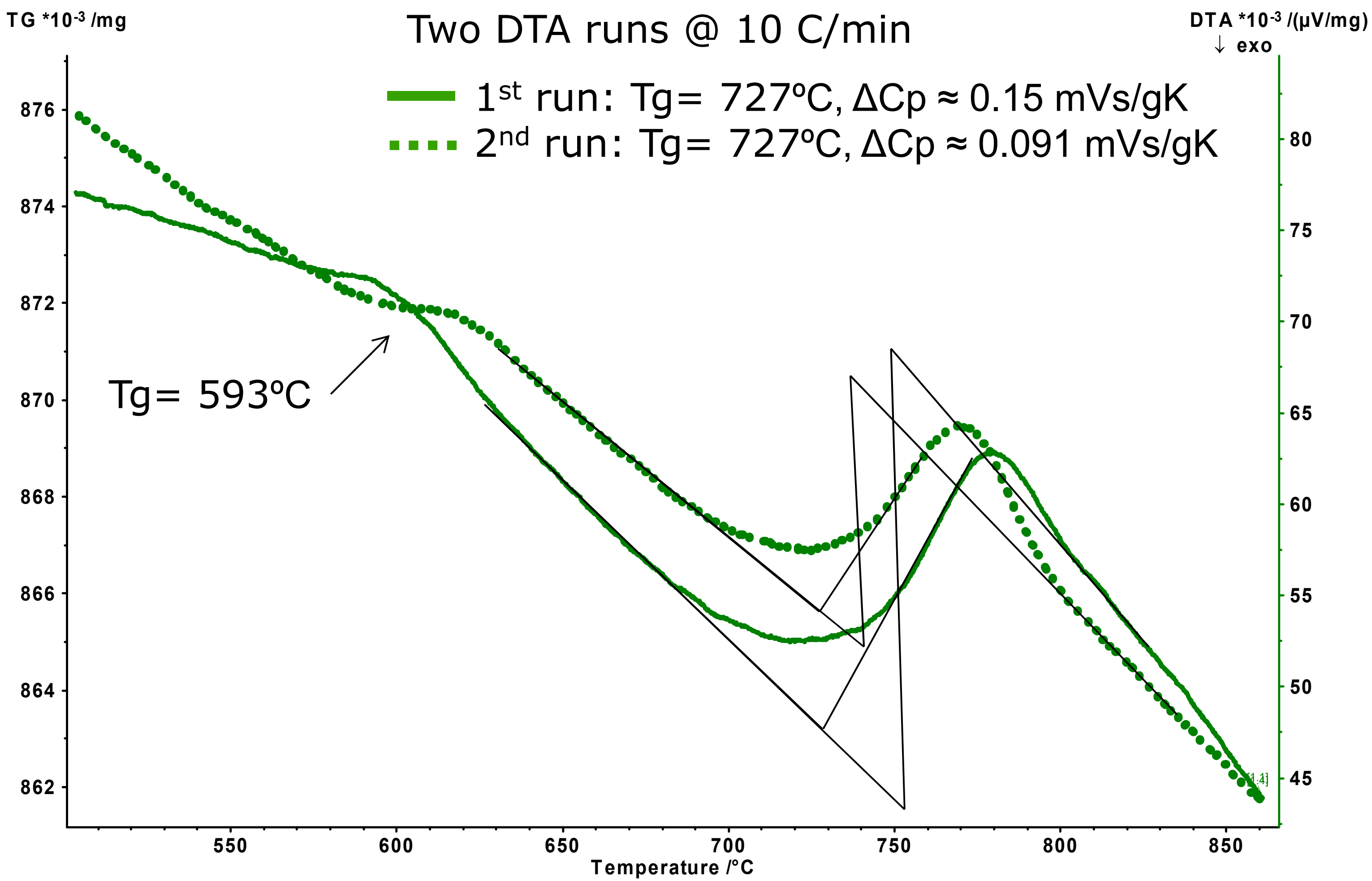
- **Using amorphous SiO_2 as filler increases the part of the glass that crystallizes to cristoballite**

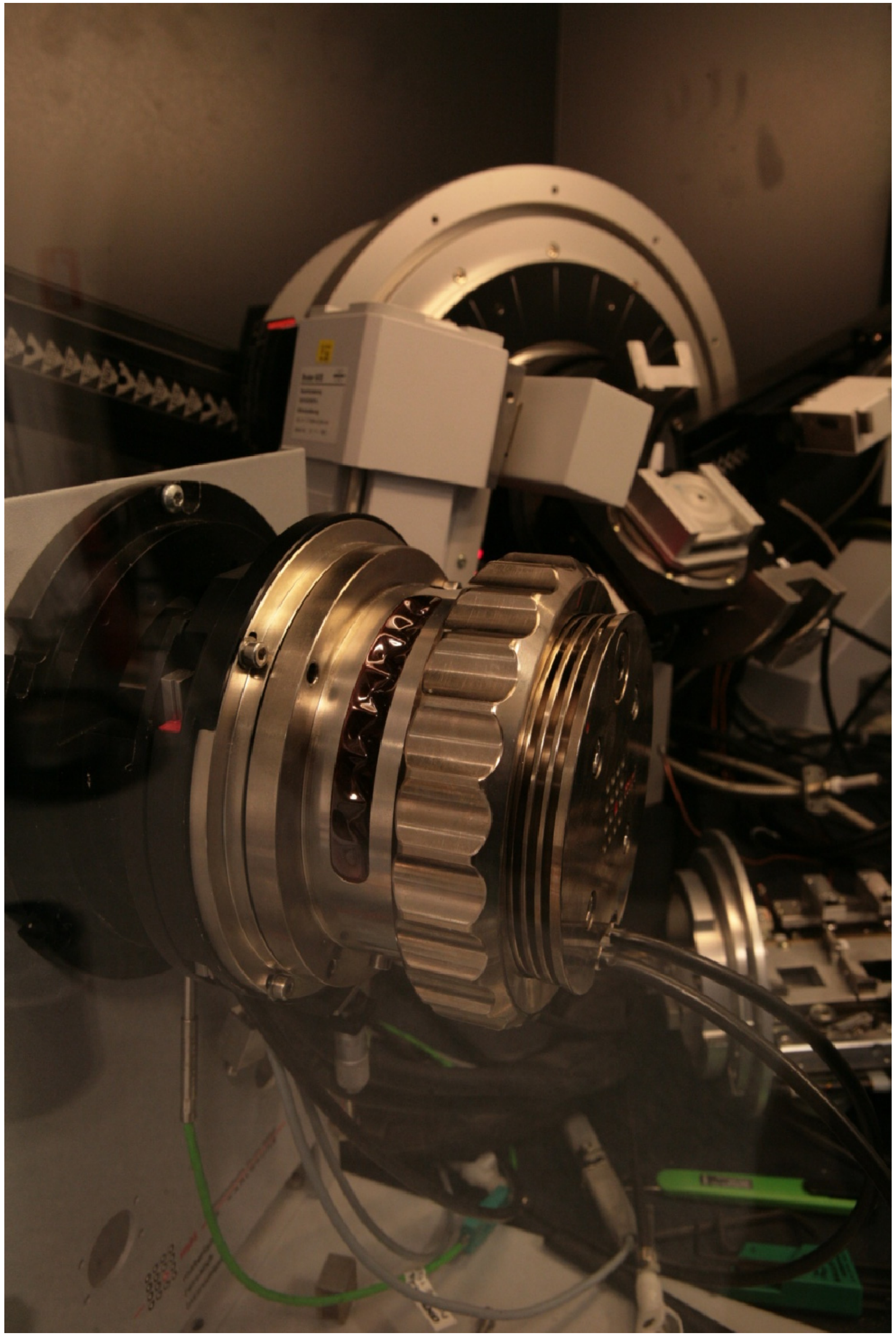
- **The CTE can be increased from 8-10 $\times 10^{-6}$ K^{-1} to about 11-12 $\times 10^{-6}$ K^{-1}**

- **Using crystalline SiO_2 as filler facilitates crystallisation of an increased amount of Quartz, which also increases CTE to desired levels**



Glass transition, Glass P





Bruker D8

with hot stage from

MRI, Karlsruhe (<1400⁰C)

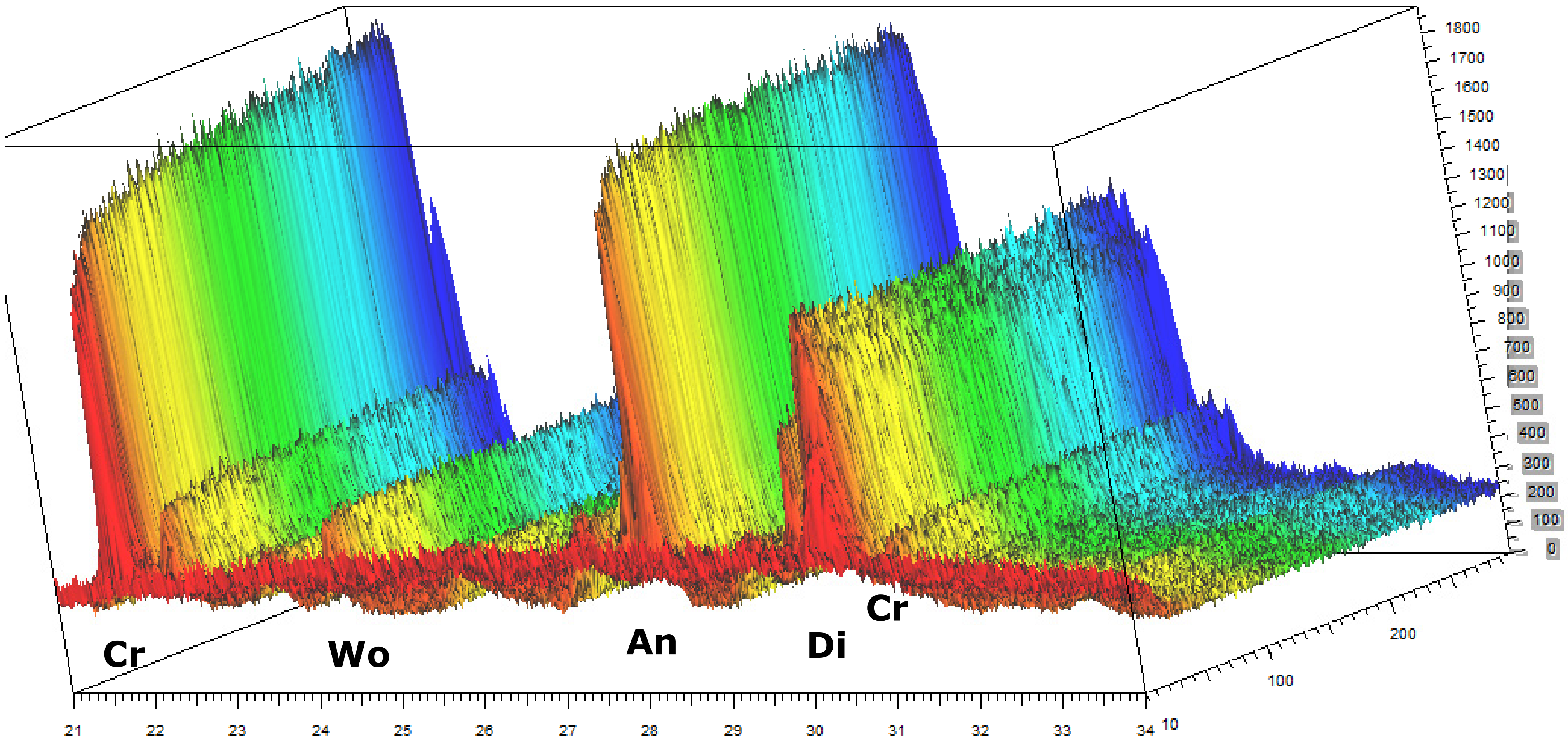
Glass P, XRD @ 900ºC for 60h

Cristobalite: SiO_2

Wollastonite: $Ca_3Si_3O_9$

Diopside: $CaMgSi_2O_6$

Anothite: $CaAl_2Si_2O_8$



Glass Sz, XRD @ 900ºC for 60h

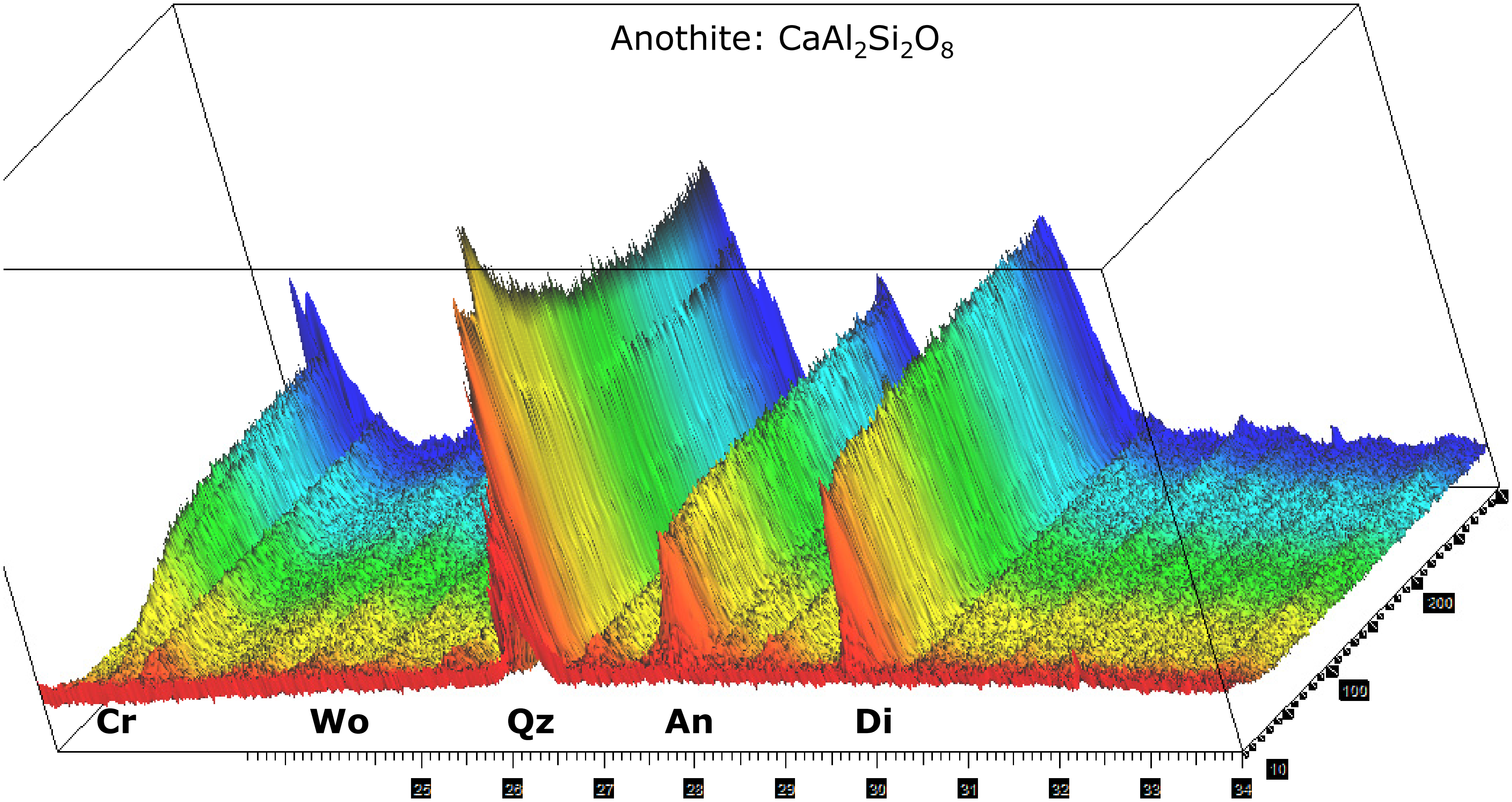
Quartz: SiO_2

Wollastonite: $Ca_3Si_3O_9$

Diopside: $CaMgSi_2O_6$

Anothite: $CaAl_2Si_2O_8$

Cristobalite: SiO_2



Conclusions

Thermal analysis encompasses a number of techniques, useful in materials research when combined.

Magneto-DSC and CATH-SPM were build to meet targeted purposes and extending the range of commercial instruments.

Optical dilatometry, or contact-free dilatometry supplements conventional TA-instruments, when looking into behaviour of multilayer ceramics.

Symmetrical instruments, DIL402CD and TG439, are efficient tools for running longer and complicated heating and gas composition profiles as when studying gas-solid reactions.

Kinetic analysis is a useful tool for acquiring rough numbers to optimise processing profiles and is at best when combined with common sense and experience.

More detailed information on crystallisation of glasses can be acquired through high temperature XRD than through DSC/DTA

Thank you for your attention

My gratitude goes to colleagues at the department, in particular to Carsten Gynter Sørensen and Pernille Hedemark for helping with experiments and to Christos Chatzichristodoulou, Stinus Jeppesen, Christian Bahl, De Wei Ni, Karin Vels and Mouritz Svendsen for sharing experimental results.